INTERACTIONS OF ANHYDROUS IRON(III) CHLORIDE WITH CHLORINE, HYDROGEN CHLORIDE AND 1,1,1-TRICHLOROETHANE

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by

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ABSTRACT

The catalytic ability of iron(III) chloride in the chlorination and hydrochlorination of hydrocarbons is well established and is of great commercial importance. Of equal importance is the dehydrochlorination of partially chlorinated ethanes, attributed to $FeCl_3$. In this work properties of $FeCl_3$ which are relevant to its catalytic behaviour were investigated.

The lability of the Fe(III)-Cl bond towards Cl_2 was investigated by performing heterogeneous reactions between $FeCl_3$ and $^{36}Cl_2$. Three types of $FeCl_3$ were used in this investigation and the surface area of each was determined by the B.E.T. method using ^{85}Kr as adsorbate. The interaction between $^{36}Cl_2$ and $FeCl_3$ was studied by two experimental techniques and the results showed that ^{36}Cl exchange between $^{36}Cl_2$ and $FeCl_3$ was not observed at room temperature under anhydrous conditions. $^{36}Cl_2$ was adsorbed by $FeCl_3$ and there was a qualitative correlation between adsorption and the surface area of $FeCl_3$.

To investigate the effect of dissolving $FeCl_3$ in a non-aqueous solvent the reaction between $FeCl_3$ and acetonitrile was examined. Previous work had shown that complexation, solvolysis and a slow reaction

to give $[Fe^{II}(CH_3CN)_6][Fe^{III}Cl_4]_2$ can occur. In the present work the $Fe^{III} \rightarrow Fe^{II}$ reduction was followed by electronic spectroscopy. The reaction was characterized by the colour changes red → orange → pale yellow and required about a week. The effect of adding chlorine to this system was studied. Chlorine was appreciably soluble in acetonitrile and $^{36}Cl_2$ underwent exchange with $FeCl_3$ readily in this solvent at 298K. Exchange was the result of chlorination of the solvent. This reaction involved solvolysis of $FeCl_3$ and an $Fe^{II}|Fe^{III}$ redox cycle. The extent of chlorination of the solvent was examined by GLC analysis. Chlorination of acetonitrile was significant and far greater than in the absence of $FeCl_3$.
The ability of $FeCl_3$ to act as a catalyst for the chlorination of acetonitrile is related to the redox cycle $Fe^{III}|Fe^{II}$ and a mechanism for this reaction is suggested.

Heterogeneous reactions between $H^{36}Cl$ and $FeCl_3$ show that ^{36}Cl exchange was not observed between anhydrous $H^{36}Cl$ and anhydrous $FeCl_3$ at room temperature. Under these conditions $H^{36}Cl$ was not adsorbed by the $FeCl_3$ surface. ^{36}Cl exchange and adsorption of $H^{36}Cl$ both occur in the presence of small quantities of water. The exchange characteristics of the reactions between $FeCl_3$ (treated with water vapour) and $H^{36}Cl$, '$FeCl_3.H_2O$' and $H^{36}Cl$ and $FeCl_3.6H_2O$ and $H^{36}Cl$ were compared.

The dehydrochlorination of 1,1,1-trichloroethane was investigated by studying the reaction between $FeCl_3$ and both unstabilized and stabilized CH_3CCl_3. The reaction between $FeCl_3$ and unstabilized CH_3CCl_3 produces vinylidene chloride and HCl. Iron(II) and Iron(III) analysis of the $FeCl_3$ showed that in the presence of light some reduction of $Fe^{III} \rightarrow Fe^{II}$ occurred. The effect on the production of vinylidene chloride and Fe^{II} of adding HCl, H_2O and CH_3CN to a mixture of $FeCl_3$ in CH_3CCl_3 was investigated. Storing mixtures of $FeCl_3$ in CH_3CCl_3 in the dark also affected the amount of vinylidene chloride produced. 36-Chlorine exchange was not observed between $H^{36}Cl$ and a mixture of $FeCl_3$ in CH_3CCl_3 under anhydrous conditions at room temperature. Addition of water to this system resulted in ^{36}Cl exchange. The interaction of $FeCl_3$ with stabilized CH_3CCl_3 showed no evidence for the production of either vinylidene chloride or HCl and ^{36}Cl exchange occurred between $H^{36}Cl$ and a mixture of $FeCl_3$ in stabilized CH_3CCl_3.

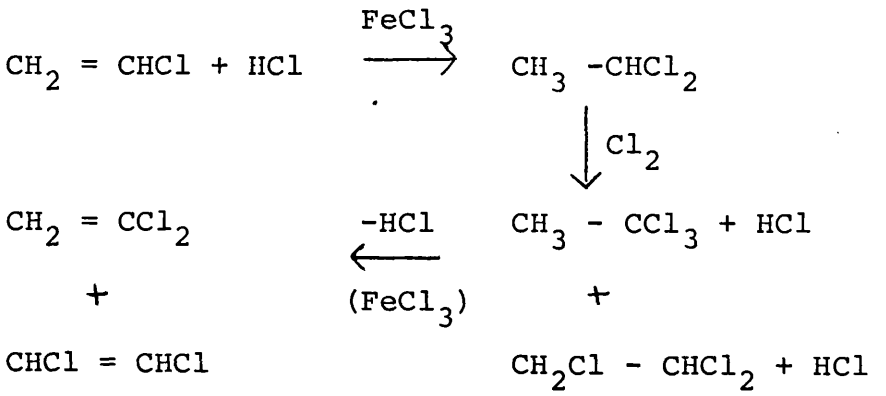
C O N T E N T S

CHAPTER ONE

CHAPTER 1

INTRODUCTION:- A SURVEY OF IRON(III) CHLORIDE'S CHEMISTRY

Metal chlorides ($FeCl_3$, $NiCl_2$, $CuCl_2$ and $AlCl_3$) are used as catalysts for the addition of Cl_2 to alkenes and alkynes and HCl to alkynes. $FeCl_3$ is of the greatest commercial importance as the chlorination of acetylene, in liquid tetrachloroethane is probably the longest established route to chlorinated hydrocarbons. Of equal importance is the dehydrochlorination of partially chlorinated ethanes which is a problem in the industrial preparation of chlorinated hydrocarbons and is also attributed to $FeCl_3$. An example of a hydrochlorination reaction is shown in reaction scheme 1. I



Scheme 1.I

The reasons for iron(III) chloride's catalytic ability are not well understood as was illustrated by an explosion which occurred during the course of this work. An iron(III) chloride plant owned by Dow Chemical in Pittsburg, California exploded, killing two and injuring 101 workers.[1]

The explosion occurred when iron(III) chloride unexpectedly decomposed to form iron(II) which reacted with the chlorinated pyridine solvent present to form tars,

regenerating the iron(III) chloride. The iron(III) chloride then reacted with some iron, forming more iron(II) chloride and thereby starting a chain reaction. One of the side-products from this reaction was hydrogen chloride, and it was the build-up in pressure due to the formation of this gas which caused the explosion.[2] Some aspects of this reaction have not been fully clarified eg. it is unclear why the iron(II) chloride was initially formed and why the chlorinated solvent, which was believed to be inert, should have participated in the reaction.

There is much in this area of chemistry which is not fully understood and this work was undertaken to investigate the role of iron(III) chloride in some of these reactions and in particular to examine the lability of the $\overset{III}{Fe}$-Cl bond.

1.1 SOLUTION CHEMISTRY OF IRON(III) CHLORIDE.

Iron(III) chloride is an effective catalyst in the preparation of chlorinated hydrocarbons. $FeCl_3$, however, is sparingly soluble in many of these reaction mixtures and there is evidence that catalysis depends on the presence of a 'co-catalyst' which dissolves the iron(III) chloride. Thus donor solvents such as water, organic-nitro compounds and, in general, organic Lewis bases should increase the catalytic activity.[3,4,5.] The reaction rate is often enhanced initially by water, but total inhibition can occur if the concentration of the co-catalyst is too high.[4] Nitroalkanes and nitrobenzenes appear both to improve the solubility of $FeCl_3$ in chloroalkanes and to increase the rate at which these reactions proceed.

1.1.1. NON-AQUEOUS SOLUTIONS.

The types of species which $FeCl_3$ exists as when dissolved in a non-aqueous solvent are important as these may be the catalytically active species. The following equilibria, based on evidence obtained by ultra-violet spectroscopy, represent different extents to which chloride ion dissociation can occur when iron(III) chloride is dissolved in a non-aqueous solvent, S.[6,7,8] (Scheme 1.II.)

$$[FeCl_3]_x + yS \longrightarrow [(FeCl_3)_xSy]$$

$$\uparrow\downarrow$$

$$0.5x\ Fe\ S_4Cl_2^+ + 0.5x\ FeCl_4^- + (y-2x)S$$

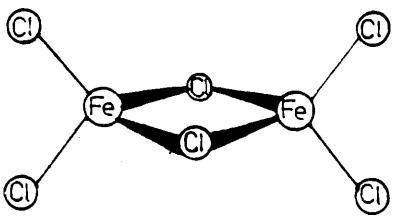
$$FeS_4Cl_2^+ \underset{Cl^-}{\overset{S}{\rightleftharpoons}} FeS_5Cl^{2+} \underset{Cl^-}{\overset{S}{\rightleftharpoons}} FeS_6^{3+}$$

Scheme 1.II

In non-aqueous solvents, the species formed will depend upon the specific properties of the solvent. The species which predominate in solution will be dependent on the donor-strength, solvating power and dielectric constant of the solvent. This means that a strong donor solvent will cause more chloride ion dissociation than a weak donor solvent. A highly polar, strongly solvating solvent will promote ionisation. The polar solvent will interact more strongly with charged ions than with $FeCl_3$ molecules. A solvent with a low dielectric constant will inhibit charge separation whilst a high dielectric constant will promote it.

The donor-strength of a solvent towards a cation is difficult to measure directly. The relative donor strengths of a solvent can be estimated by comparing enthalpy data obtained from the gas phase or a poorly solvating solvent. When a series of similar ligands are used information on the size of the metal ion-ligand interaction can be gained from the spectrochemical parameter Dq. The solvating properties of a solvent can be estimated by comparing the association constant, Kas, for tetraalkylammonium halides in the solvents of interest. Useful information can also be gained by comparing the Z values of the solvents.[9] These are measures of the effect solvation has on the energy of the charge-transfer transition of an N- substituted pyridinium ion.

From these considerations it can be seen that the choice of solvent will determine the iron species formed in solution. The existence of the Fe_2Cl_6 dimer has been reported in the vapour phase [10] (Formula 1.I) but despite claims that the dimer exists in non-donor solvents such as benzene, toluene and ether,[11] it has been shown that in these solvents the type of species is $[(FeCl_3)_xSy]$.[12,13]



Formula 1.I

In these solvents $FeCl_3$ is photosensitive and upon irradiation reacts with the solvent yielding $FeCl_2$ and chlorinating the solvent.[12].

In a recent Mössbauer study[14], it was established that iron(III) chloride exists solely in the dimeric or polymeric forms in benzene and nitrobenzene. In acetone, acetonitrile, pyridine and dimethylformamide both monomeric and dimeric (or oligomeric) solvates exist, whilst in ethanol only the monomeric form exists. This investigation, however, was performed on samples which were frozen immediately after being prepared and would therefore only give information on the species initially formed in solution. If the equilibria reactions of complexation through to solvolysis are established slowly then this investigation gives no information on the final species formed in solution.

It has also been reported that iron(III) chloride exists as the dimer in concentrated solutions of methanol.[15] This was established by X-ray techniques which compared the radial-distribution functions of the $FeCl_3$ - methanol solutions with those from an electron-diffraction study of vapour-phase Fe_2Cl_6. Another investigation in which the ultraviolet spectra of this solution were examined stated that both FeS_5Cl^{2+} and $FeS_4Cl_2^+$ exist in solution.[8] Methanol is a complex solvent since it is capable of extensive hydrogen bonding interactions. As it is a good donor solvent it would seem more likely that dissociation of iron(III) chloride would occur in this solvent. At the moment, therefore, there is no conclusive evidence in the literature for the existence of the Fe_2Cl_6 dimer in solution.

The solvent equilibria, shown in Scheme 1.II are very dependent on the solvent used. Dimethylsulphoxide has a

sufficiently high dielectric constant to lead to solute ionization and is a fairly good Lewis base. It is expected to exhibit good donor ability towards the metal ion, good anion solvation and to be capable of supporting ionization. It has been shown, by spectroscopic measurements, that when iron(III) chloride is dissolved in dimethylsulphoxide, (DMSO), the main species present are $[Fe(DMSO)_5Cl]^{2+}$ and Cl^-. An X-ray structure determination has been performed on crystals obtained from a solution of anhydrous iron(III) chloride in DMSO. These crystals were composed of trans-$[FeCl_2(DMSO)_4]^+$ and $FeCl_4^-$ ions.[16] The species which exist in solution, however, are not necessarily the same as these in the solid state. In N-methyl formamide, a solvent with slightly less donor ability but which is a very good solvating solvent, $FeCl_3$ exists primarily as $Fe(NMA)_6^{3+}$ and Cl^-.[8] Acetonitrile is a weak donor, of moderate solvating ability and the main species present in this solvent are $[Fe(CH_3CN)_4Cl_2]^+$ and $FeCl_4^-$.[17]

The solution chemistry of $FeCl_3$ is further complicated in some solvents by the reduction of Fe^{III} to Fe^{II} and the chlorination of the solvent. A slow reduction of $FeCl_3$ occurs in acetonitrile and after a week at room temperature $[Fe^{II}(CH_3CN)_6]$ $[Fe^{III}Cl_4]_2$ can be isolated from solution.[18] The structure of crystals obtained from a solution of iron(III) chloride in acetonitrile has been obtained and found to contain two tetrahedra ($Fe^{III}Cl_4^-$) and one octahedron $[Fe^{II}(CH_3CN)_6]^{2+}$.[19] The extent of the reduction from Fe^{III} to Fe^{II} is influenced by metal chlorides. When strong chloride ion acceptors such as antimony penta-

chloride are added to a solution of $FeCl_3$ in acetonitrile then complete reduction from Fe^{III} to Fe^{II} occurs and the species formed is $[Fe^{II}(CH_3CN)_6][SbCl_6]_2$. The addition of a chloride ion donor, example LiCl, causes no reduction of Fe(III) to Fe(II) and the species formed is $Li(CH_3CN)_4(FeCl_4)$.[20] The explanation offered for these incomplete reductions is that when $FeCl_3$ is dissolved in acetonitrile, the species formed in solution are $Fe(CH_3CN)_4Cl_2^+$ and $FeCl_4^-$. The cation, $Fe(CH_3CN)_4Cl_2^+$ is much more easily reduced than the tetrachloroferrate ion and results in only one-third of the iron being reduced to Fe^{2+}. It would appear that Fe^{3+} is only stable in acetonitrile when it is surrounded by four chloride ions as the introduction of strong chloride ion acceptors resulted in the complete reduction of the iron(III) whereas chloride ion donors effectively stopped the reduction. It has been shown that the compound $[Fe(CH_3CN)_6][FeCl_4]_2$ can be prepared directly from iron wire and chlorine in acetonitrile.[21] (Equation 1.I).

$$3Fe + 4Cl_2 + 6CH_3CN \longrightarrow [Fe^{II}(CH_3CN)_6][Fe^{III}Cl_4)_2$$

Equation 1.I.

It has been suggested that nitromethane behaves in a similar manner to acetonitrile when used as a solvent for iron(III) chloride.[22] In the partial reduction of iron, chlorination of the solvent must occur with evolution of HCl, but this aspect of the reaction was not studied. Chlorination of acetonitrile by other transition metal chlorides has been reported and it is known that a number

of metal chlorides are reduced to a lower oxidation state of the metal when reacted in excess acetonitrile. Vanadium(IV) chloride forms the complex $VCl_4 2CH_3CN$ when reacted with acetonitrile in a carbon tetrachloride solution but when reacted directly in an excess of acetonitrile, the vanadium is reduced and $VCl_3 3CH_3CN$ is formed.[23] This reaction also occurred in other alkyl cyanide solutions, RCN where R = Et, Pr^n. In this reaction HCl is evolved which implies that chlorination of the solvent has occurred. Although the oxidation products are not fully investigated, when only a slight excess of acetonitrile is used the infrared spectrum of the volatile liquid shows C-Cl stretching frequencies. This indicates that some chlorination of the acetonitrile has occurred.

When molybdenum(V) chloride, tungsten(VI) and tungsten(V) chloride are dissolved in acetonitrile, they are completely reduced.[24]

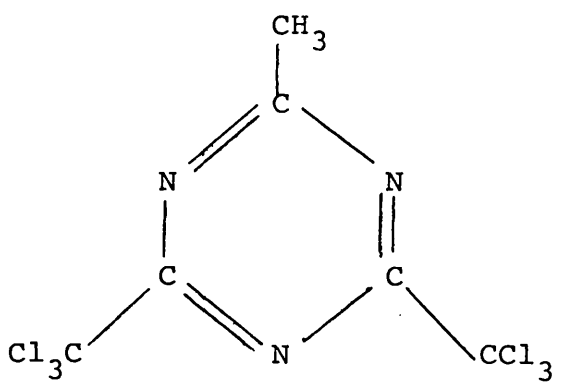
1. $MoCl_5$ gave $MoCl_4(CH_3CN)_2$
2. WCl_6 gave $WCl_4(CH_3CN)_2$
3. WCl_5 gave $WCl_4(CH_3CN)_2$

The oxidation products from these reactions were not identified but it was noted that on removal of all the volatile material, the infrared spectrum showed no evidence of any halogenated species. It was suggested in both these papers that as hydrogen chloride was formed, a hydrogen atom must have been abstracted from the acetonitrile thus leaving the radical $\cdot CH_2CN$ which could dimerise or initiate further polymerisation. It was noted that hydrogen chloride can form the unstable compound

$[CH_3CNH]^+[HCl_2]^-$ on reaction with acetonitrile.

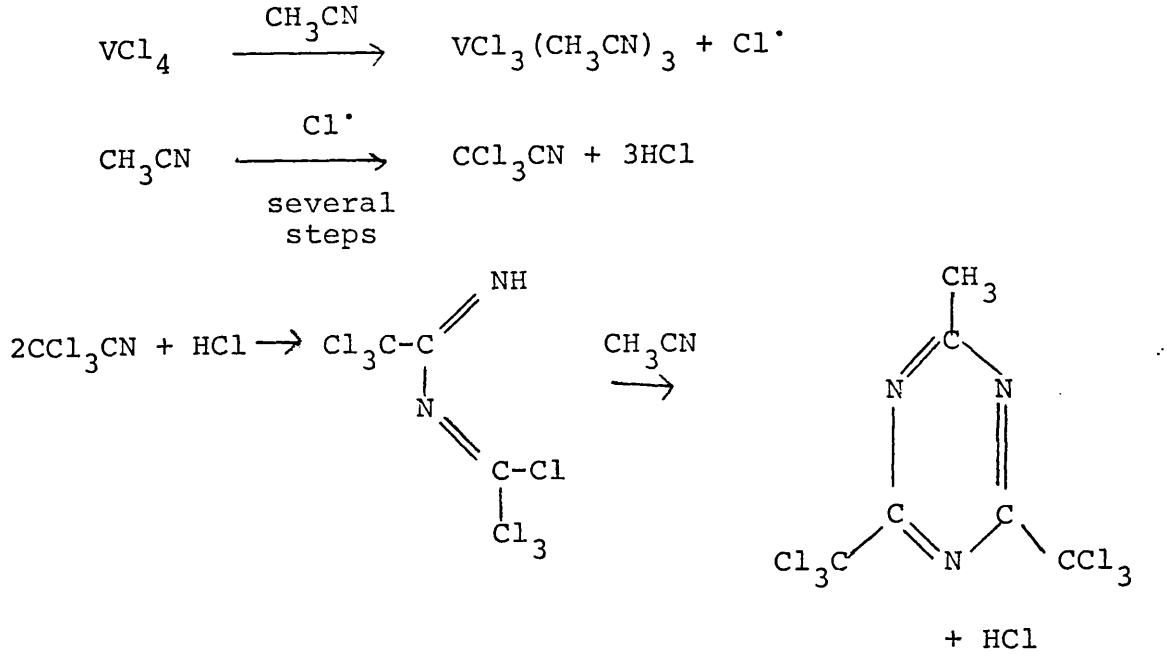
In the reduction of $ReCl_5$ to $ReCl_4(CH_3CN)_2$ in the presence of acetonitrile, the oxidation products were examined.[25] After extraction of the reaction products, an oil was isolated with an empirical formula of $C_{8.5}H_7NCl_2$ and a molecular weight of 240 in benzene. This molecular weight neither corresponds to, nor is it a multiple of, the empirical formula which suggests that a mixture of compounds has been isolated. An infrared spectrum was recorded and contained bands due to the C-Cl stretching frequencies.

The main organic oxidation product has been fully characterized in only one instance, the reaction between VCl_4 and excess acetonitrile. The product was identified by chemical analysis, mass spectrum, infrared spectrum and NMR spectroscopy and found to be 2-methyl-4,6-bis(trichloromethyl)-1,3,5-triazine. (Formula 1.II)[26]



Formula 1.II

The mechanism proposed for the formation of this product is shown in scheme 1.III



Scheme 1.III

Only the final product from this reaction scheme was actually characterized and no evidence was given for the formation of CCl_3CN or of CH_2ClCN, which would be a reasonable precursor. The initial stages in this reaction, therefore, are not clear.

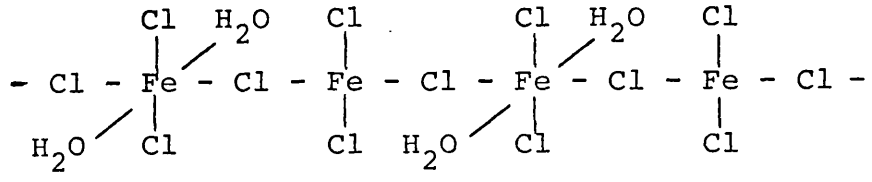
The reverse process to the reduction of transition metal chlorides by acetonitrile is the ability of monochloro, dichloro and trichloroacetonitrile to oxidise and complex with various transition metal chlorides.[27,28] Both tungsten(V) and tungsten(VI) chloride react to give the same complex, $WCl_6.2CCl_3CN$ on treatment with trichloroacetonitrile. ie. tungsten(V) has been oxidised to tungsten(VI) in the presence of CCl_3CN. X-ray work has shown that this compound exists as trans-$[(CCl_3CN)WCl_4(NCCl_2CCl_3)]$.[29] Titanium(III) chloride can be oxidised by

mono-, di- and trichloroacetonitrile yielding the compounds $TiCl_4.2CH_2ClCN$, $TiCl_4.2CHCl_2CN$ and $TiCl_4.CCl_3CN$ respectively. Treatment of the trichloroacetonitrile complexes with a small amount of acetonitrile causes replacement of the trichloroacetonitrile ligands by acetonitrile ligands. This means that even in systems where acetonitrile is oxidised to the CCl_3CN, only the acetonitrile complex would be observed in the presence of even a slight excess of acetonitrile.

1.1.2. AQUEOUS SOLUTIONS.

It is extremely difficult to obtain anhydrous iron(III) chloride and, therefore, water is often a contaminant in the reaction mixtures of iron(III) chloride in chlorohydrocarbons. The type of species which $FeCl_3$ exists as in an aqueous solution is of some importance. Many investigations have been carried out on aqueous solutions and some conflicting results have been obtained. I.R., U.V. and Mössbauer spectra obtained from neutral solutions of iron(III) chloride suggest that a complicated polymeric structure is formed.[30] In highly acidic solutions, evidence from U.V. spectra suggests that the predominant species is the $FeCl_4^-$ anion.[31] X-ray diffraction techniques have also been used to investigate these solutions. Standley and Kruh[32] found the tetrachloroferrate ion, $FeCl_4^-$, is the principal species in acidic solutions. They also suggest that $FeCl_4^-$ is the predominant species in neutral solutions. They do point out, however, that this would require that chlorines are shared between iron atoms. Brady et. al.[33] found that in concentrated acidic solutions a polymeric

species is formed. This consisted of alternating $FeCl_4$ and $FeCl_4(H_2O)_2$ units, with adjacent units sharing a chloride ion. (Formula 1.III)



Formula 1.III

This polymer only occurs in concentrated solutions and on dilution with concentrated HCl, the tetrachloroferrate ion is formed in solution. (Equation 1.II)

$$[FeCl_4\ FeCl_2\ (H_2O)_2]_x + 2xCl^- \longrightarrow 2xFeCl_4^- + 2xH_2O.$$

Equation 1.II

In neutral solutions they suggest that the main species is $FeCl_4(H_2O)_2^-$ and that this is surrounded by a hydration sheath.

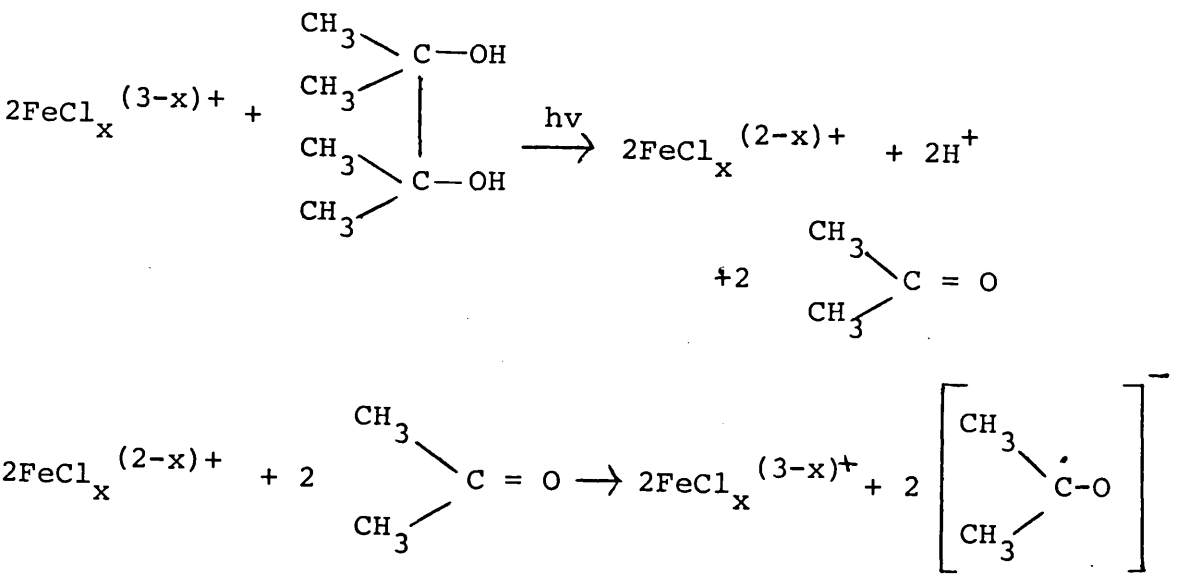
A detailed investigation has been carried out by examining the Raman spectra obtained from ferric chloride hexahydrate in the melt, in neutral and in acidic solutions.[34] From this it was concluded that the structure of $FeCl_3.6H_2O$ differs in the crystalline state, in the melt and in solution. In the crystalline state $FeCl_3.6H_2O$ exists as $[FeCl_2(H_2O)_4^+]Cl^-.2H_2O$ and the crystal structure of this has been determined.[35] There are, of course, other hydrates of iron(III) chloride and the iron(III) chloride - water phase diagram reveals four hydrates. These are $FeCl_3.2H_2O$, $FeCl_3.2\frac{1}{2}H_2O$, $FeCl_3.3\frac{1}{2}H_2O$ and $FeCl_3.6H_2O$. The crystal structure of $FeCl_3.2\frac{1}{2}H_2O$ has

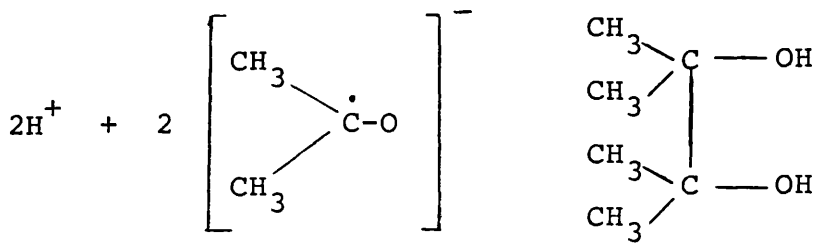
also been obtained and consists of a distorted tetrahedral $FeCl_4^-$ anion, a distorted octahedral tetraquo-cis-dichloro-iron(III) cation and a single solvate water molecule, that is $[FeCl_2(H_2O)_4]^+.[FeCl_4^-].H_2O$.[36] From Raman spectra it was interpreted that in the melt, $FeCl_3.6H_2O$ exists predominantly as $FeCl_4^-$ and $Fe(H_2O)_4Cl_2^+$ ions. When the melt is saturated with dry HCl or LiCl, all the $Fe(H_2O)_4Cl_2^+$ ions are converted to $FeCl_4^-$, and the only species present is $FeCl_4^-$. The type of species present in solution depend on the concentration of solution. Thus in both concentrated neutral and moderately acidic solutions a polymeric species exist. This consists of higher chloroferrates, $FeCl_5.H_2O$ and $FeCl_6$ randomly orientated in a polymeric network along with significant concentrations of $Fe(H_2O)_4Cl_2^+$ and $Fe(H_2O)_5Cl^{2+}$. The stability of this species is dependent on the temperature and water content of the system though a strong hydration sheath surrounds the polymeric species and lends stability to the complex. When these solutions are saturated with dry HCl, the polymer is completely converted into $FeCl_4^-$. On dilution, dissociation of the polymeric species occurs resulting in the formation of $Fe(H_2O)_4Cl_2^+$, $Fe(H_2O)_5Cl^{2+}$ and even $Fe(H_2O)_6^{3+}$. This is thought to be due to the strong competition of water molecules with the Cl^- ions.

1.2 Fe^{II}/Fe^{III} PHOTOREACTIONS.

There are many instances in the literature of redox Fe^{II}/Fe^{III} reactions, where irradiation of $FeCl_3$ solutions by UV light results in the oxidation of the organic solvent.

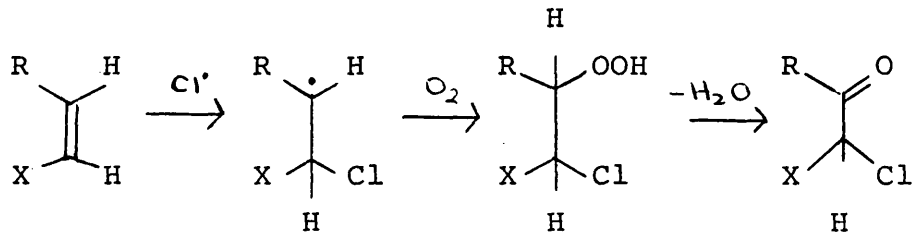
On irradiation, a solution of iron(III) chloride with pinacol in acetonitrile results in the photoreduction of Fe^{III} to Fe^{II} and the concomitant oxidation of pinacol to acetone.[37] Acetone is the only oxidation product and is obtained at nearly 100% yield based on the amount of ferric chloride which is present. When water is used as solvent in place of acetonitrile no reaction takes place. Presumably this is due to water forming strong hydration complexes with iron(III) chloride which stops the reduction of Fe^{III} to Fe^{II}. It has been shown in an acetone solution of anhydrous iron(III) chloride and pinacol that after irradiation has ceased, all the Fe^{II} present is spontaneously oxidised back to Fe^{III}.[38] In this process all the Fe^{III} is recovered. This cycle, which was repeated three times, consists of the photochemical reduction of Fe^{III} to Fe^{II} and then the thermal oxidation of Fe^{II} to Fe^{III}, and was shown to be photochromic. The mechanism proposed for these reactions are shown in scheme 1.IV.





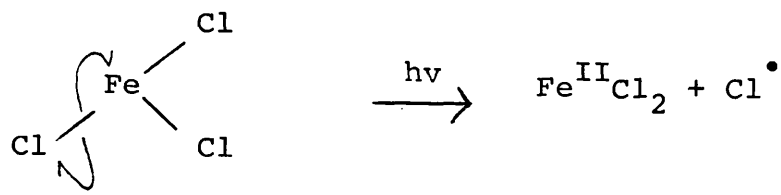
Scheme 1.IV

When oxygen is bubbled through a solution of iron(III) chloride in pyridine and the solution is irradiated, this reacts with mono- and di-substituted olefins to give α-chloroketones and with tri and tetra-substituted olefins to give dichloroketones.[39] The scheme postulated for this type of reaction is shown in scheme. lV.



Scheme lV

It was noted that no reaction took place in the dark. Presumably this reaction is initiated by iron(III) chloride reacting, on irradiation, to give iron(II) chloride and a chlorine radical. (Scheme 1.VI) The chlorine radical would subsequently react with the olefin.



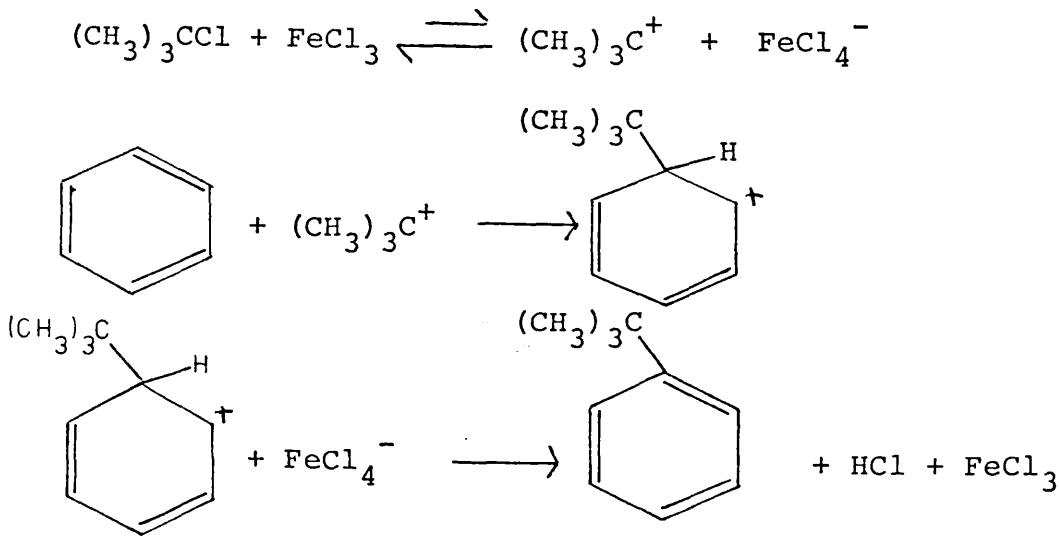
Scheme 1.VI

Interestingly, it was noticed that if these reactions were performed in the presence of a chlorinated solvent, for

example CCl_4 or $CHCl_3$, then iron(III) chloride behaved as a catalyst. In this case, a chlorine radical from CCl_4 could oxidise the Fe^{II} back to Fe^{III}.

1.3 FRIEDEL - CRAFTS REACTIONS.

A Friedel-Crafts reaction is any substitution, isomerization, elimination, cracking, polymerization or addition reaction which takes place under the catalytic influence of Lewis acid acidic halide or proton acid.[40] The ability of iron(III) chloride to accept electrons pairs and act as a Lewis acid is well established and its ability to function as a Friedel-Crafts reagent was first cited in 1877.[41] $FeCl_3$ is a milder catalyst than $AlCl_3$ and is useful for reactions where $AlCl_3$ causes decomposition. An example of $FeCl_3$ as a Friedel-Crafts' reagent is shown in this Friedel-Crafts' alkylation. (scheme 1.VII) In this substitution reaction, $FeCl_3$ is being used to produce a carbonium ion.



Scheme 1.VII

1.4. CHLORINATED SOLVENTS.

Chlorinated hydrocarbons are used extensively as cleaning solvents. They have many applications and can be used to clean a wide variety of substances ranging from heavy industrial cleaning to dry-cleaning of clothes. Their usefulness as cleaning solvents is due to their low intermolecular attractions which gives them solubility parameters similar to those of oil and greases.[42] In the UK they are made exclusively by ICI Ltd. The solvents most commonly used are trichloroethylene $CHCl = CCl_2$, tetrachloroethylene $CCl_2 = CCl_2$, 1,1,1-trichloroethane CH_3CCl_3 and methylene chloride CH_2Cl_2. The EEC commission has estimated the yearly demand of these solvents to be:-

$CHCl = CCl_2$	tonnes per year
$CCl_2 = CCl_2$	combined > 300,000
$CH_3\ CCl_3$	200,000
$CH_2\ Cl_2$	250,000

Transition metal chlorides are used as catalysts in the preparation of these solvents. There are three main ways in which they function as catalysts.

1. They can display their lewis acid ability and act as electron pair acceptors
2. They can act as free radical inhibitors in chlorine substitution reactions. (scheme 1.VIII)

$$FeCl_3 + Cl. \longrightarrow FeCl_2 + Cl_2$$
$$FeCl_3 + RH^{\cdot} \longrightarrow FeCl_2 + HCl + R$$

Scheme 1.VIII

3. They can act as oxychlorination catalysts. This

applies particularly to $CuCl_2$. (scheme 1.IX)

$$2\ CuCl_2 + CH_2 = CH_2 \longrightarrow 2\ CuCl + CH_2ClCH_2Cl.$$

$$2\ CuCl + \tfrac{1}{2}O_2 \longrightarrow Cu\ O\ CuCl_2$$

$$Cu\ O\ CuCl_2 + 2HCl \longrightarrow CuCl_2 + H_2O$$

Scheme 1.IX

Iron(III) chloride is frequently used as a catalyst in the preparation of these chlorinated hydrocarbons as it can catalyse chlorination, hydrochlorination and dehydrochlorination reactions.

1.4.1. CHLORINATION REACTIONS

In the presence of chlorine, iron(III) chloride can function as a chlorination catalyst, though it is also possible for $FeCl_3$ to chlorinate hydrocarbons in the absence of chlorine. The chlorination of acetylene by $FeCl_3$ is performed in liquid tetrachlorethane and is an established route in the production of chlorinated hydrocarbons. (Equation 1.III)

$$C_2H_2 + Cl_2 \xrightarrow[1,1,2,2,\ C_2H_2Cl_4]{FeCl_3} 1,1,2,2,\ C_2H_2Cl_4.$$

Equation 1.III

Originally, $FeCl_3$ was prepared 'in situ' by the direct chlorination of scrap iron. Under the conditions used little chlorination of the iron occurred unless the solvent contained traces of water. Water may be necessary to oxidise the iron or it may be functioning as a co-catalyst whose role is to produce a protic acid. Later

$FeCl_3$ was used directly in the chlorination of acetylene to give tetrachloroethane. The reaction rate was dependent on the specific surface area of the $FeCl_3$[43]. A poisoning effect was noted if too high a concentration of water was present in this reaction mixture. This could be overcome by increasing the concentration of iron(III) chloride used.[44] This poisoning effect is probably due to the removal of $FeCl_3$ by hydrolysis.

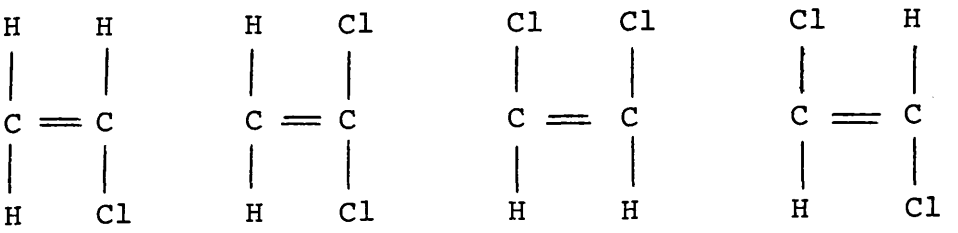
Iron(III) chloride is used as a catalyst for the chlorination of ethylene to give 1,2,dichloroethane. The mechanism suggested for this reaction is that $FeCl_3$ functions as a Lewis acid and causes heterolytic cleavage of the chlorine.[42] (scheme 1.X)

$$FeCl_3 + Cl_2 \longrightarrow [FeCl_4^-]Cl^+ \longrightarrow [FeCl_4^-]^+CH_2CH_2Cl \downarrow CH_2ClCH_2Cl + FeCl_3$$

Scheme 1.X

Iron(III) chloride can also inhibit the production of radical chains which lead to over-chlorination by reacting with chlorine atoms to give chlorine and ferrous chloride. In the presence of only 100 ppm ferric chloride almost the sole product of ethylene chlorination is 1,2,dichloroethane.

The cationic polymerisation of vinyl chloride (Formula 1.IV), vinylidene chloride (Formula 1.V) and 1,2 dichloroethylene (Formula 1.VIA + 1.VIB) can be promoted by iron(III) chloride, particularly in the presence of moisture.[45] In the case of vinyl chloride, this is achieved by the formation of



Formula 1.IV | Formula 1.V | Formula 1.VIA | Formula 1.VIB

the reactive carbonium ion CH_3^+CHCl, which like other carbonium ions initiate further polymerisation of vinyl chloride,[46] with the formation of oligomeric and polymeric products.

Benzene can be chlorinated by iron(III) chloride in the presence of chlorine though water plays an important role in this reaction. Some work has been carried out to determine the influence of water on the reaction rate of benzene catalysed by $FeCl_3$ in a homogeneous reaction medium.[3] It was concluded that iron(III) chloride monohydrate ie. $FeCl_3.H_2O$ was the active catalyst species. If the water content of the system was increased to give a higher hydrate species then a poisoning effect was observed. The greater catalytic ability of $FeCl_3.H_2O$ compared to $FeCl_3$ was linked to the fact that $FeCl_3.H_2O$ is more soluble in benzene. It has been determined that the higher hydrates are also less soluble in benzene than the monohydrate.[47] In the production of 1,2 dichloroethane, obtained by introducing chlorine and ethylene into a catalyst solution in 1,2 dichloroethane, a similar conclusion was established.[48] The efficiency of $FeCl_3.H_2O$ as a catalyst over $FeCl_3$ or the higher hydrates was again greater and this was also linked to its increased solubility

in the organic solvent. As already stated, apart from catalysing the chlorination by a polar mechanism, the catalyst functions as a free-radical inhibitor. Traces of water, therefore, would be beneficial in helping to maintain the $FeCl_3$ concentration.

1.4.2. DECHLORINATION REACTIONS.

The dechlorination of chlorohydrocarbons is catalysed by ferrous chloride. The oxidation of iron(II) chloride by carbon tetrachloride in acetonitrile has been studied spectrophotometrically and leads to the formation of iron(III)chloride and tetrachloroethylene.[49] In this reaction trichloromethyl radicals are captured by iron(II) chloride to give a carbenoid complex which decomposes into iron(III) chloride and tetrachloroethane. (scheme 1.XI)

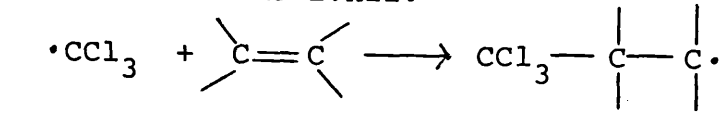
$$Fe^{2+} + CCl_4 \rightleftharpoons FeCl^{2+} + \cdot CCl_3$$

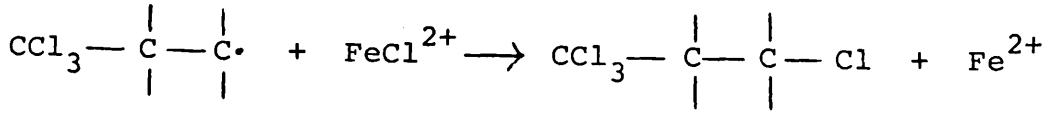
$$Fe^{2+} + \cdot CCl_3 \rightleftharpoons Fe(CCl_3)^{2+}$$

$$2\ Fe(CCl_3)^{2+} \longrightarrow 2\ FeCl^{2+} + C_2Cl_4$$

Scheme 1.XI

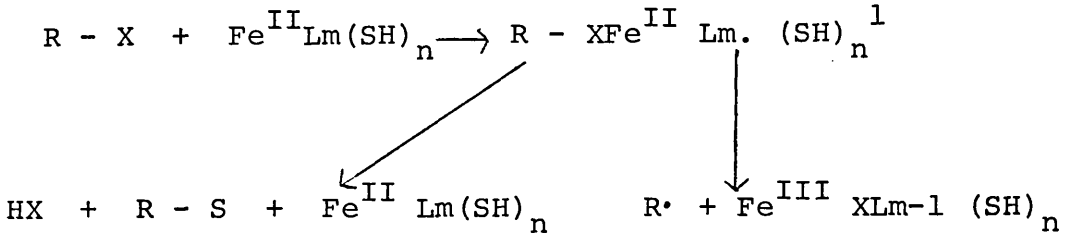
If this reaction is carried out in the presence of an olefin, then the $.CCl_3$ radical can react with the olefin as shown in scheme 1.XII.





Scheme 1.XII

A solution of iron(II) chloride in dimethylsulphoxide (DMSO) brings about the dechlorination of organic halides.[50] In this iron(II) chloride tetrahydrate is dissolved in DMSO and reacted with benzylic or alkylic halides. The reaction mechanism proposed is shown in scheme 1.XIII



where L = DMSO, H_2O

X = HALIDE ION

SH = protonic solvent.

Scheme 1.XIII

The R• radicals, which are formed by the halide iron salt complex undergoing a one-electron transfer, can recombine to give the product R-R.

1.4.3. HYDROCHLORINATION REACTIONS.

The most important industrial hydrochlorination reactions involve addition of HCl to vinyl chloride, vinylidene chloride and 1,2 dichloroethylene. Iron(III) chloride is an efficient catalyst for hydrochlorination but is not very soluble in chlorohydrocarbons, therefore, the catalyst is used as a slurry. For example the hydrochlorination of vinylidene chloride to give 1,1,1-trichloroethane (Equation 1.IV) uses a slurry of anhydrous iron(III) chloride in perchloroethylene. The catalyst is

$$CH_2 = CCl_2 + HCl \xrightarrow{FeCl_3} CH_3 - CCl_3$$

Equation 1.IV

difficult to handle and causes blockages in the reactor. It was noticed that in high local concentrations of the catalyst, polymerisation of the vinylidene chloride occurred. It is known that in the presence of stronger Lewis acids, eg. $AlCl_3$, polymerization of vinylidene chloride occurs readily.[45] To overcome the problems of a heterogeneous reaction, reactions are often performed in which the iron(III) chloride has been dissolved in a donor solvent.

However in some of these solvents, for example, 1,4 dioxan and CH_3CN, the complex formed inhibits the hydrochlorination reaction. Nitroalkanes and nitrobenzenes are efficient both at increasing the solubility of $FeCl_3$ in chloroalkanes and in increasing the rate of hydrochlorination[4]. The role of iron(III) chloride as a catalyst for this reaction is thought to involve ionization of HCl, followed by protonation of vinylidene chloride with subsequent addition of chloride ion to give 1,1,1-trichloroethane.

1.4.4. DEHYDROCHLORINATION REACTIONS.

Chloroethanes can decompose with the loss of hydrogen chloride (Equation 1.V)

$$RCHCl.CH_2R' \rightleftharpoons RCH = CHR' + HCl$$

Equation 1.V

It is desirable to drive the equilibrium to the left-hand side and to increase the stability of chloroethanes.

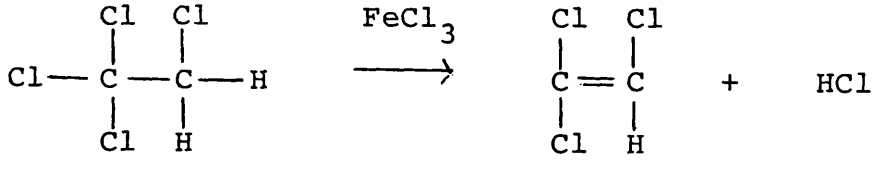
It is necessary to add stabilizers which prevent the loss of HCl. Hydrogen chloride is more readily lost from non-symmetric chloroethanes. For chloroethanes which contain a $CHCl_2$ group, the thermal stability of the compound increases with the degree of chlorination of the neighbouring methyl group ie.

$$CH_3CHCl_2 < CH_2ClCHCl_2 < CHCl_2CHCl_2.$$

However, the stability drops on going to pentachloroethane ie. CCl_3CHCl_2. Chloroethanes which contain a methyl group are also more stable as the degree of chlorination of the neighbouring group increases

$$CH_3CH_2Cl < CH_3CHCl_2 < CH_3CCl_3.$$

Dehydrochlorination reactions can be performed by thermal cracking, by base or in the presence of iron(III) chloride as catalyst. In the latter case the dehydrochlorination (Equation 1.VI) has been carried out in the liquid phase with an excess of solid $FeCl_3$ present.[5]



Equation 1.VI

Although it is thought that these reactions are homogeneous, it is necessary to have some excess solid iron(III) chloride present. Nitroethane and 1 - nitropropane increase the solubility of $FeCl_3$ in tetrachloroethane and also increase the rate of dehydrochlorination of 1,1,1,2-

tetrachloroethane. In the reaction scheme proposed (scheme 1.XIV), it is suggested that the co-catalyst solvates the $FeCl_3$. However the complex which is formed, must be capable of at least partial dissociation to produce the catalytic species.

$$Fe_2Cl_6 + 2m\ EtNO_2 \longrightarrow 2\ FeCl_3\ (Et\ NO_2)_m$$

$$FeCl_3\ (EtNO_2)_m \rightleftharpoons FeCl_3\ (EtNO_2)_{m-n} + n\ EtNO_2$$

$$R - Cl + FeCl_3\ (EtNO_2)_{m-n} \longrightarrow [R^+ + FeCl_4\ (EtNO_2)^-_x]$$

$$[R^+ + FeCl_4\ (EtNO_2)^-_x] \longrightarrow \text{olefin} + FeCl_3\ (EtNO_2)_{m-n} + HCl$$

Scheme 1.XIV

This scheme does not explain why it is necessary to have solid $FeCl_3$ present in the reaction but a possibility is that the solid $FeCl_3$ removes any impurities for example water.

The importance of iron(111)chloride in the preparation of chlorohyrocarbons is well established but its role is not clear in many cases.

CHAPTER TWO

CHAPTER 2 - EXPERIMENTAL

In this work, it was important to ensure that all moisture and air were excluded from reactions examined, since water can function as a co-catalyst with iron(III) chloride.[3,4] All the work was, therefore, performed in vacuo (10^{-4} mm Hg) or in an inert atmosphere box ($H_2O \leq 10$ ppm) and every precaution was taken to exclude water.

2.1 EQUIPMENT.

2.1.1. THE VACUUM SYSTEM.

The vacuum line (Figure 2.I) was an enclosed pyrex glass structure which was pumped by means of a mercury diffusion pump and an oil-sealed rotary pump to a pressure of 10^{-5} mm. Hg. The pumps were, protected from any volatile material in the line, by waste traps. These were situated directly before the pumps and were long glass tubes surrounded by liquid nitrogen which trapped any volatile substance. The vacuum line consisted of a manometer, a vacustat and the main manifold. The manometer was used to measure the pressure of liquids and gases contained in the line, while the vacustat was used to measure the pressure which the pumping system achieved. The main manifold consisted of various outlets to which rotaflo vessels, of the type shown in Figure 2.II, were attached. These rotaflo vessels were made of pyrex glass and had a side-arm. They were sealed off from

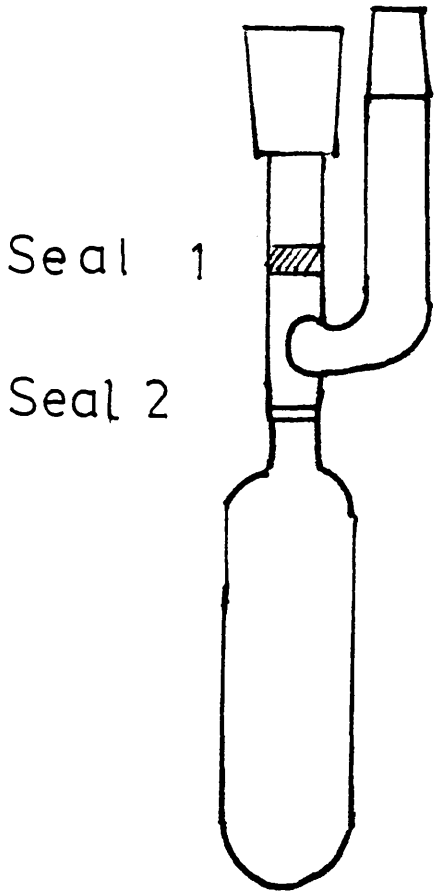


Figure 2II

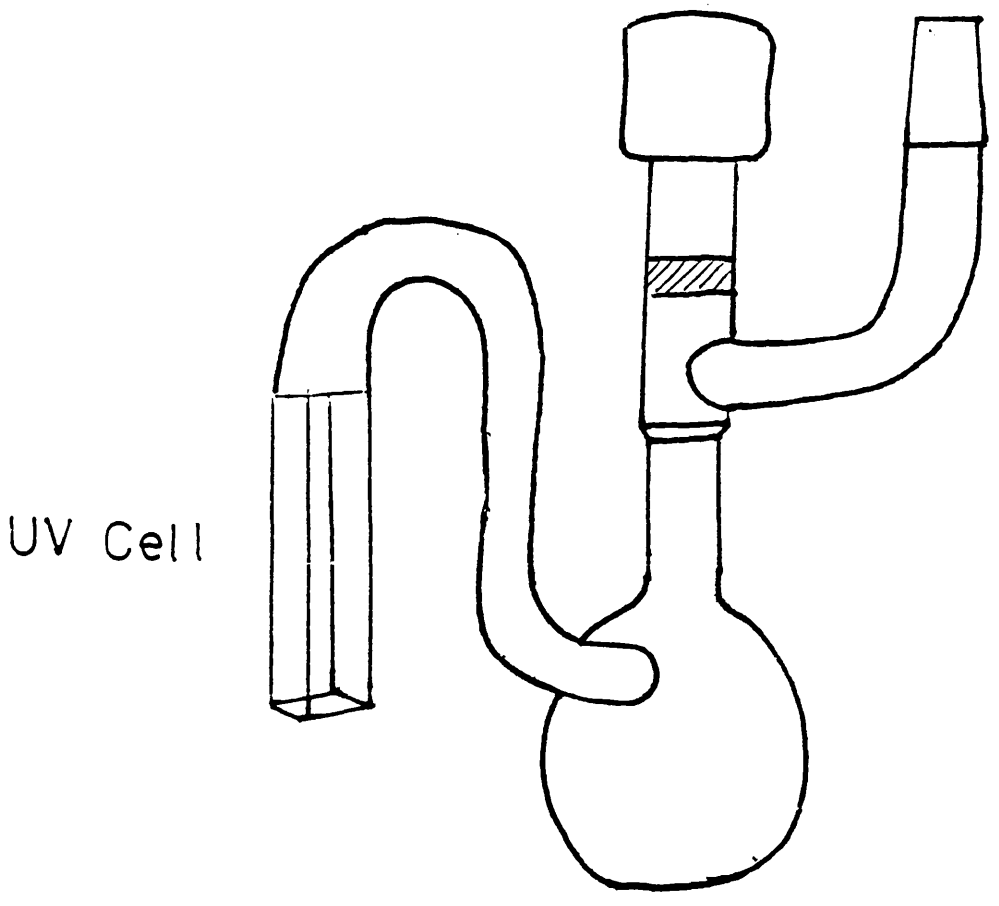


Figure 2III

the atmosphere by a rotaflo tap. This tap was made of PTFE and when screwed into a glass vessel made a continuous seal with the glass (Figure 2.II, Seal 1). A further seal was made by tightening an inner screw in the rotaflo tap (Figure 2.II, Seal 2). Operations could thus be performed, from one vessel to another, in a dry atmosphere, by opening seal 1 and keeping seal 2 closed.

To further ensure that all moisture adsorbed on to the surface of the glass was removed, the glass vessels and the line were flamed out with a gas/oxygen flame while the system was pumped.

2.1.2. THE INERT ATMOSPHERE BOX.

An argon atmosphere Lintott box ($H_2O \leq 10$ ppm) was used when handling and storing all samples. Glass vessels used were previously evacuated and flamed out before being transferred to the box. The box contained a balance which allowed samples to be weighed in this dry atmosphere. All solutions and samples were prepared in this box.

2.1.3. ELECTRONIC SPECTROSCOPY.

Electronic spectra were recorded on a Beckman Spectrophotometer UV 5270, using the UV cell shown in Figure 2.III. This consisted of a quartz UV cell joined by a glass limb to a small rotaflo vessel. Solutions were prepared accurately in the inert atmosphere box and degassed twice before recording the spectra. Solutions were degassed by being cooled to 77K and then pumped.

2.1.4. INFRARED SPECTROSCOPY

The IR work was performed on a Perkin-Elmer (577) Grating Infrared Spectrophotometer. Both the solution and gas IR cells had KBr windows.

2.2. PREPARATION OF CHEMICALS

2.2.1. PREPARATION OF $FeCl_3$.

Three types of $FeCl_3$ have been used in an attempt to characterize any differences in their surface areas and in their exchange behaviour. These were

a) $FeCl_3$ prepared by the passage of Cl_2 over iron wire,

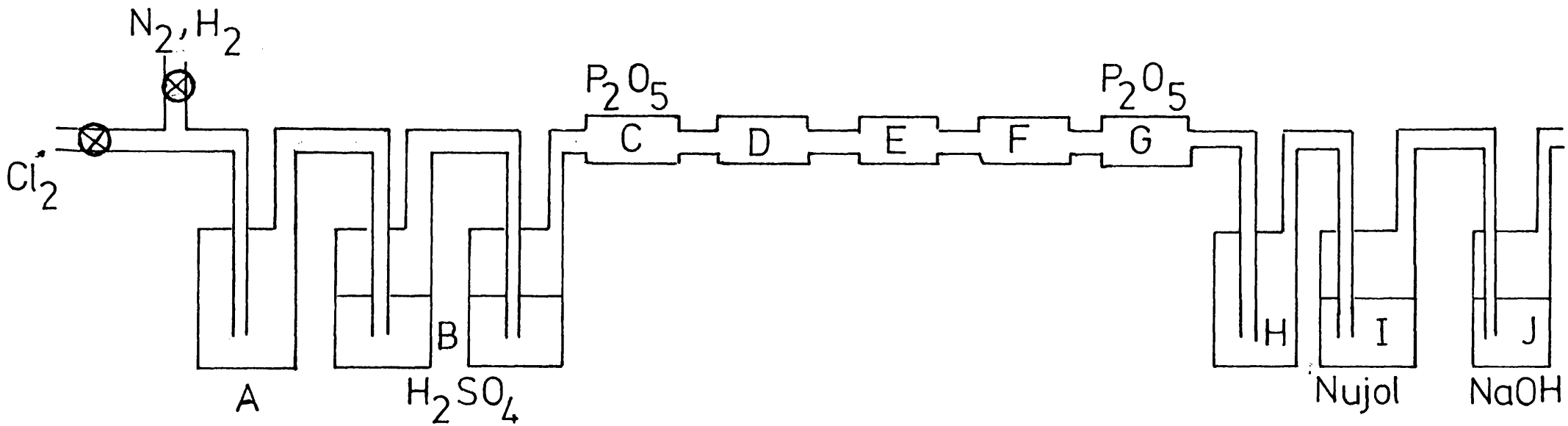
b) $FeCl_3$ prepared by $SOCl_2$ dehydration of $FeCl_3.6H_2O$,

c) Commercial $FeCl_3$ (anhydrous)

METHOD A. PREPARATION OF $FeCl_3$ FROM Fe(WIRE) + Cl_2.[51]

$$2Fe + 3Cl_2 \rightarrow 2FeCl_3 \quad \text{..... Eq. 2.I.}$$

The apparatus used is shown in Figure 2.IV. The glass reaction vessel consisted of three compartments, D, E and F, which were joined by constricted segments. The reaction vessel was surrounded by a furnace whose temperature could be controlled. Before entering the reaction vessel, the gases were passed through an empty bubbler (A), to prevent splash-back, an H_2SO_4 bubbler (B) and a drying tube containing phosphorus (V) oxide (C). After the reaction vessel, the gases were passed through another phosphorus (V) oxide drying tube(G), an empty bubbler (H) and finally a bubbler containing nujol (I),



Preparation of $FeCl_3$-

Figure 2IV

used to detect any blockages in the system. When chlorine was passed through this system an extra bubbler (J) containing NaOH was added to prevent any release of chlorine gas to the atmosphere.

Iron wire (Goodfellow Metals, % Purity 99.99+) was placed in the compartments D, E and F. Before the reaction was performed, the reaction vessel was flamed out and the iron wire reduced by passing hydrogen gas over it at 473K for 24h. After this, the system was flushed out with nitrogen, which was dried by passage through activated molecular sieves (Type 4A) and a cold trap held at 195K by solid CO_2. Chlorine gas was passed over the iron wire at 473K leading to the formation of green crystals of $FeCl_3$ in the reaction compartments D, E and F. These were sealed by melting the glass at the constricted segments of the reaction vessel and stored in an inert atmosphere box.

ANALYSIS	OBTAINED:-	Fe 33.9%	Cl 65.1%
	REQUIRED:-	Fe 34.43%	Cl 65.57%

METHOD B. PREPARATION OF $FeCl_3$ FROM $SOCl_2$ DEHYDRATION OF $FeCl_3.6H_2O$.[52]

$$FeCl_3.6H_2O + 6SOCl_2 \longrightarrow FeCl_3 + 6SO_2 + 12HCl \quad \ldots\ldots \text{Eq. 2II}$$

Finely ground iron(III) chloride hexahydrate (20g; 0.074 mmol) was placed in a round-bottomed flask and

50ml of freshly distilled thionyl chloride added at room temperature. Sulphur dioxide and hydrogen chloride were immediately evolved. After the bubbling stopped, the slurry was refluxed for 1-2h, the flask attached to the vacuum line and excess thionyl chloride removed. The $FeCl_3$ obtained was pumped for several hours before being transferred to the inert atmosphere box.

METHOD C. COMMERCIAL $FeCl_3$ (anhydrous).

This sample was provided by ICI Ltd., Mond Division and was made on a bulk industrial scale.

2.2.2. PREPARATION OF TETRAETHYLAMMONIUM TETRACHLOROFERRATE.[53]

The salt was precipitated by adding $[(C_2H_5)_4N]Cl.H_2O$ (0.6426g; 3.50 mmol) in 12M HCl to a 12M HCl solution of iron(III) chloride (0.4975g; 3.01 mmol). The yellow crystals obtained were filtered, washed with 12M HCl and dried by suction before being transferred to a vacuum line where they were pumped overnight.

ANALYSIS

OBTAINED:- C 29.4%, H 6.0%, N 4.2%, Cl 43.3%

REQUIRED:- C 29.3%, H 6.15%, N 4.3%, Cl 43.25%.

2.2.3. PREPARATION OF 36-CHLORINE.

The main considerations in the preparation of $^{36}Cl_2$ were to produce anhydrous $^{36}Cl_2$ with a high specific activity. The uncertainty in a count N is $\sqrt{N}$. If an

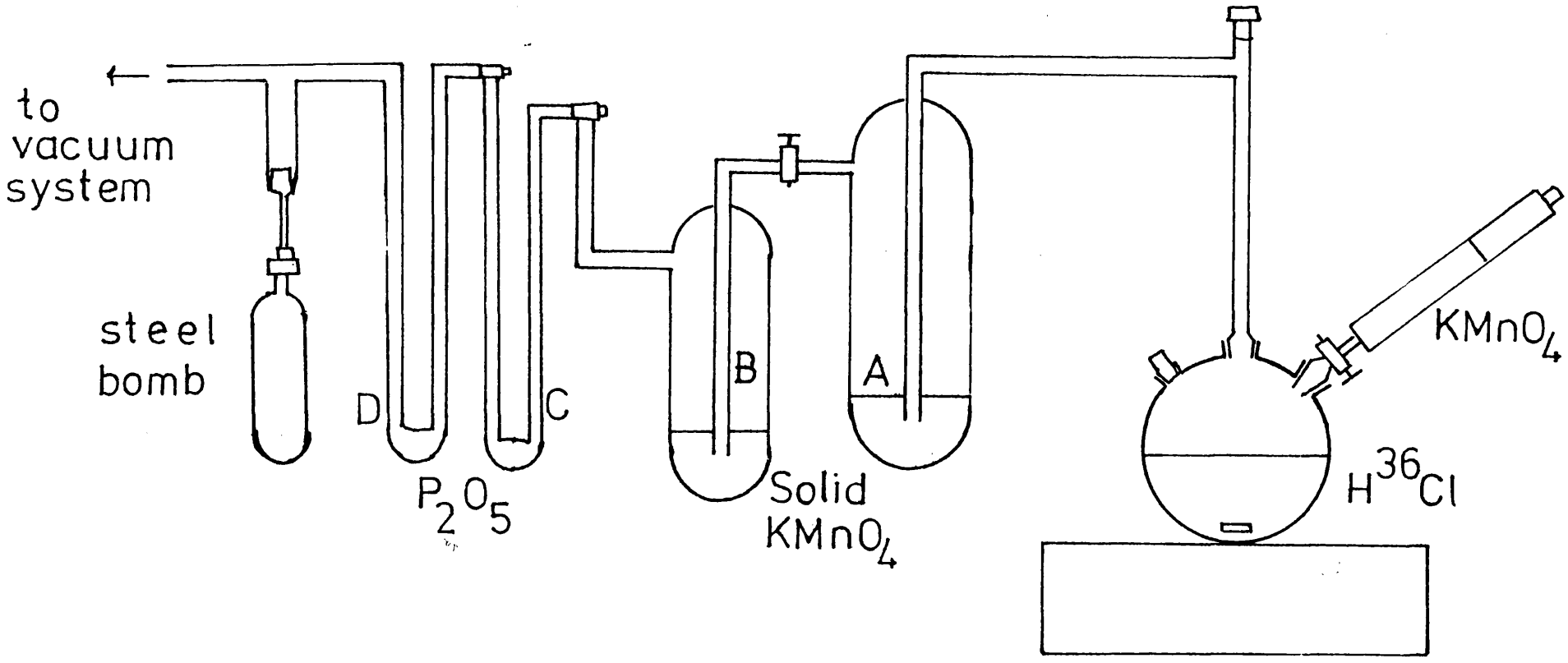
active sample can produce 10^4 counts, this leads to an uncertainty of only 1%. In exchange reactions, in case of fast exchange, it is desirable to monitor the system at short intervals. The sample, therefore, must be sufficiently active to produce a large number of counts in a short counting time. The preparation of $^{36}Cl_2$ was carried out by the following procedure using the apparatus shown in Figure 2.V.

$$KMnO_4 + 4H^{36}Cl \rightarrow K^{36}Cl + MnO_2 + 2H_2O + 3/2\,^{36}Cl_2 \quad \ldots\ldots \text{Eq. 2.III}$$

The ground-glass joints in the apparatus were sealed with Kel-F wax and the whole system, apart from the three-neck flask, was evacuated before the reaction. 0.55 ml of 0.1 - 0.3 M H ^{36}Cl (50 μCi, Radiochemical Centre) was diluted with 100 ml 2M HCl and placed in a three neck round-bottom flask. A solution of 2M $KMnO_4$ was added dropwise and the mixture stirred. The chlorine liberated was distilled through traps A and B at 77 K. These traps contained solid $KMnO_4$ which removed any HCl still present. The chlorine was then distilled through traps C and D, which contained P_2O_5, to remove any moisture present. The $^{36}Cl_2$ was collected and stored in a pre-evacuated steel bomb which contained P_2O_5.

2.2.4. PREPARATION OF HYDROGEN 36-CHLORIDE.

The main considerations were to produce anhydrous $H^{36}Cl$ with a high specific activity. This proved more difficult than with $^{36}Cl_2$ and two techniques were used.



Preparation of $^{36}Cl_2$

Figure 2V

METHOD A.

Sodium chloride (11.1146g; 0.1902 mol.) was dissolved in 50 ml of distilled water and 0.55 ml of 0.1 - 0.3M $H^{36}Cl$ (50 μCi, Radiochemical Centre) was added. After mixing, the solution was placed under an infrared lamp for several hours to obtain crystals of $Na^{36}Cl$. The $Na^{36}Cl$ was transferred to a rotaflo flask and pumped under vacuum for 48h. The flask was removed to a dry box where the $Na^{36}Cl$ was transferred to a stainless steel bomb. Anhydrous HCl gas (0.5128g; 0.0141 mol) was distilled into the bomb, which was then held at 353K for 48h. The $H^{36}Cl$ gas was removed and its activity determined.

This method produced very dry $H^{36}Cl$ but with a low specific activity. (87 ± 8 count $(600sec)^{-1}$ mg^{-1}).

METHOD B.

This was adapted from a literature method[54] to suit the radiochemical purpose.

$$H^{36}Cl \text{ aq.} + H_2SO_4 \rightarrow H^{36}Cl + H_2SO_4 \quad \text{.....Eq. 2.IV.}$$

$H^{36}Cl$ was produced using the apparatus shown in Figure 2.VI. This consisted of a 50ml dropping funnel which was sealed to a capillary tube and a 500 ml separating funnel. The separating funnel was connected by glass tubing to a Woolfe bottle which contained concentrated sulphuric acid. This was connected by a glass outlet to a 350 ml rotaflo vessel in which the gas produced was collected.

$H^{36}Cl$ Generator

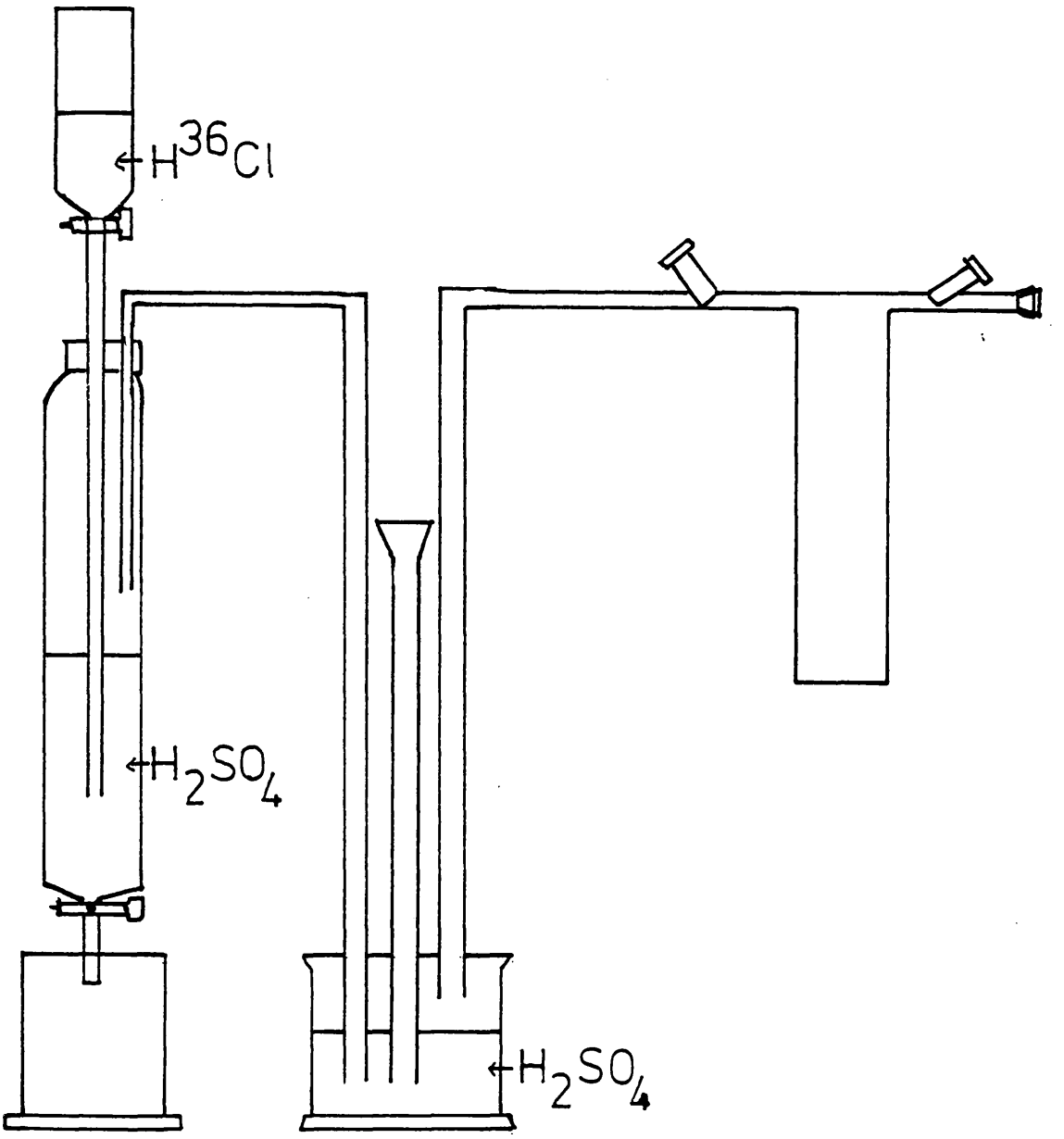


Figure 2VI

Hydrogen 36-chloride was produced by mixing 0.55 ml 0.1-0.3 M $H^{36}Cl$ (50μCi, Radiochemical Centre) with 5 ml of concentrated HCl. This was placed in the dropping funnel. When the solution of $H^{36}Cl$ was added dropwise to the separating funnel, containing 75 ml of concentrated H_2SO_4, gaseous $H^{36}Cl$ was produced and collected in the rotaflo vessel at 77K.

This method produced rather wet $H^{36}Cl$ with a high specific activity. (736 ± 33 count (600 sec)$^{-1}$ mg^{-1})

2.3. ANALYTICAL TECHNIQUES.

2.3.1. ANALYSIS OF CHLORINE AND HYDROGEN CHLORIDE.

To determine their specific activities, $^{36}Cl_2$ and $H^{36}Cl$ were converted to $Ag^{36}Cl$ and counted in the solid phase. The activity balance in a reaction should be $\geq$ 95%, therefore the conversion procedure should be carried out with an efficiency $\geq$95%. The procedure used was adapted from a literature method[55] to suit the radiochemical purpose.

$$\left.\begin{array}{l} {}^{36}Cl_2 + 2NaOH \rightarrow Na^{36}Cl + NaO^{36}Cl + H_2O \\ H_{36}Cl + NaOH \rightarrow Na^{36}Cl + H_2O \end{array}\right\}$$

$$NaO^{36}Cl + H_2O_2 \rightarrow Na^{36}Cl + H_2O + O_2$$

$$Na^{36}Cl + AgNO_3 \rightarrow Ag^{36}Cl + NaNO_3.$$

$^{36}Cl_2$ was distilled into a slight excess of sodium hydroxide in vacuo. The solution was removed to a beaker by several washings of water. A calculated amount of hydrogen peroxide was added to convert all the NaOCl to

sodium chloride. The solution was acidified with 1 ml of 1:1 nitric acid. Silver chloride was precipitated by the slow addition of a slight excess of silver nitrate solution and the suspension heated to just below boiling for approximately two hours. The solution was set aside and allowed to cool.

A filter crucible was washed with an alcohol/ether solution, dried under suction for ten minutes and placed in a desiccator for a further twenty minutes before it was weighed. The precipitate of $Ag^{36}Cl$ was collected in this weighed filter crucible, washed with small portions of 0.01M nitric acid followed by distilled water before being dried by the procedure outlined above.

The same conversion procedure was used for $H^{36}Cl$. This conversion procedure was carried out with an efficiency $\geq$95% for both $^{36}Cl_2$ and $H^{36}Cl$. (Table 2.I)

CONVERSION OF $^{36}Cl_2$ AND $H^{36}Cl$ TO $Ag^{36}Cl$.

	$Ag^{36}Cl$ Obtained g	$Ag^{36}Cl$ Required for Complete Conversion g	% Efficiency
$^{36}Cl_2$ (0.0270g)	0.1062	0.1090	97.4
$H^{36}Cl$ (0.0153g)	0.0580	0.0602	96.3

TABLE 2.I

2.3.2. ANALYSIS OF IRON(III) CHLORIDE.

The purity of $FeCl_3$ samples was checked by the following method.[56]

A sample of $FeCl_3$ was dissolved in 50 ml distilled water and 5 ml concentrated nitric acid and the solution heated to boiling. A solution of ammonia was then slowly added with stirring until an excess of NH_3 was present as indicated by the odour. A small amount of ashless filter paper was then added to coagulate the precipitate. The solution was removed from the heat, filtered and washed with hot 1% ammonium nitrate followed by distilled water. A porcelain crucible was ignited, allowed to cool for 1h. in a desiccator and weighed. The precipitate was placed in the crucible and this procedure repeated. In this way the amount of Fe_2O_3 recovered was accurately determined.

All the washings were kept and the chloride ion precipitated as AgCl by adding an excess of $AgNO_3$ as outlined in section 2.3.1.

Both the iron and chloride analysis were carried out with an efficiency $\geq$95%. (Table 2.II)

ANALYSIS OF IRON(III) CHLORIDE

SAMPLE	CHLORIDE		%	IRON		%
	% Obtained	% Required	Efficiency	% Obtained	% Required	Efficiency
$FeCl_3$ (0.1526g)	63.8	65.6	97.2	34.1	34.4	98.9

TABLE 2.II

The specific activity of the chloride ion in active samples of $FeCl_3$ was determined as silver chloride.

2.3.3. ANALYSIS OF IRON'S OXIDATION STATE.[57]

Iron(II) can be determined spectrometrically as the 2-2' bipyridyl complex $(C_5H_4N)_2$. The Fe (bipyridyl)$_3^{2+}$ ion gives a strong absorbance with its ϵmax = 522 nm. A quantitative method for determining the amount of Fe^{II} present in a sample involved converting all the Fe^{II} to the Fe (bipyridyl)$_3^{2+}$ ion. A calibration curve was obtained by measuring the absorbance of varying concentrations of Fe(bipyridyl)$_3^{2+}$ at the λmax. The calibration curve was obtained using Analar ammonium iron(II) sulphate. A series of solutions containing between 1-25 mg Fel^{-1} was prepared. A 10 ml aliquot of each of these solutions was pipetted into a 100 ml conical flask, followed by 10 ml of 1 MHCl and the mixture boiled for five minutes. Five ml of 10% w/w hydroxylamine hydrochloride solution was added and the flask heated for five minutes to ensure all the iron was present as Fe^{II}. The solution was neutralised with 2 ml ammonia, boiled for a further five minutes and allowed to cool. The solution was buffered by the addition of 10 ml 20% w/w ammonium acetate before 2 ml of 0.1% 2-2' bipyridyl was added to complex the Fe^{II}. The solution was made up to 50 ml with distilled water. The calibration curve, obtained from plotting the iron concentration against the absorbance,

is shown in Figure 2.VII and it obeys the Beer-Lambert Law over the concentration range used.

To determine the amount of Fe^{II} and Fe^{III} present in a sample, a solution was prepared from which two separate 10 ml aliquots were taken. The method outlined above was followed but hydroxylamine hydrochloride was only added to one of the solutions to convert all the iron present to Fe^{II}. The iron(II) present, in both solutions, was then converted to $Fe(bipyridyl)_3^{2+}$. The absorbance from the solution, to which hydroxylamine hydrochloride was added, was due to the total amount of iron present in the initial sample, whereas in the other solution it was due only to the amount of Fe^{II} present in the initial sample.

This method was used to determine the amount of total iron, of Fe^{II}, and hence by difference, the amount of Fe^{III} in a solution.

2.4. PURIFICATION METHODS.

2.4.1. PURIFICATION OF HYDROGEN CHLORIDE.

This method was used to purify and dry both active and inactive hydrogen chloride.

Impure HCl in its solid form at 77K has a 'rose-red' colour.[58] The HCl was purified by warming to 143K in a n-pentane slush bath and distilling it into a trap held at 77K. The distillate was further distilled from a 40% ether - 60% ethanol slush bath at 133K over a 2.5h period into a trap at 77K. The

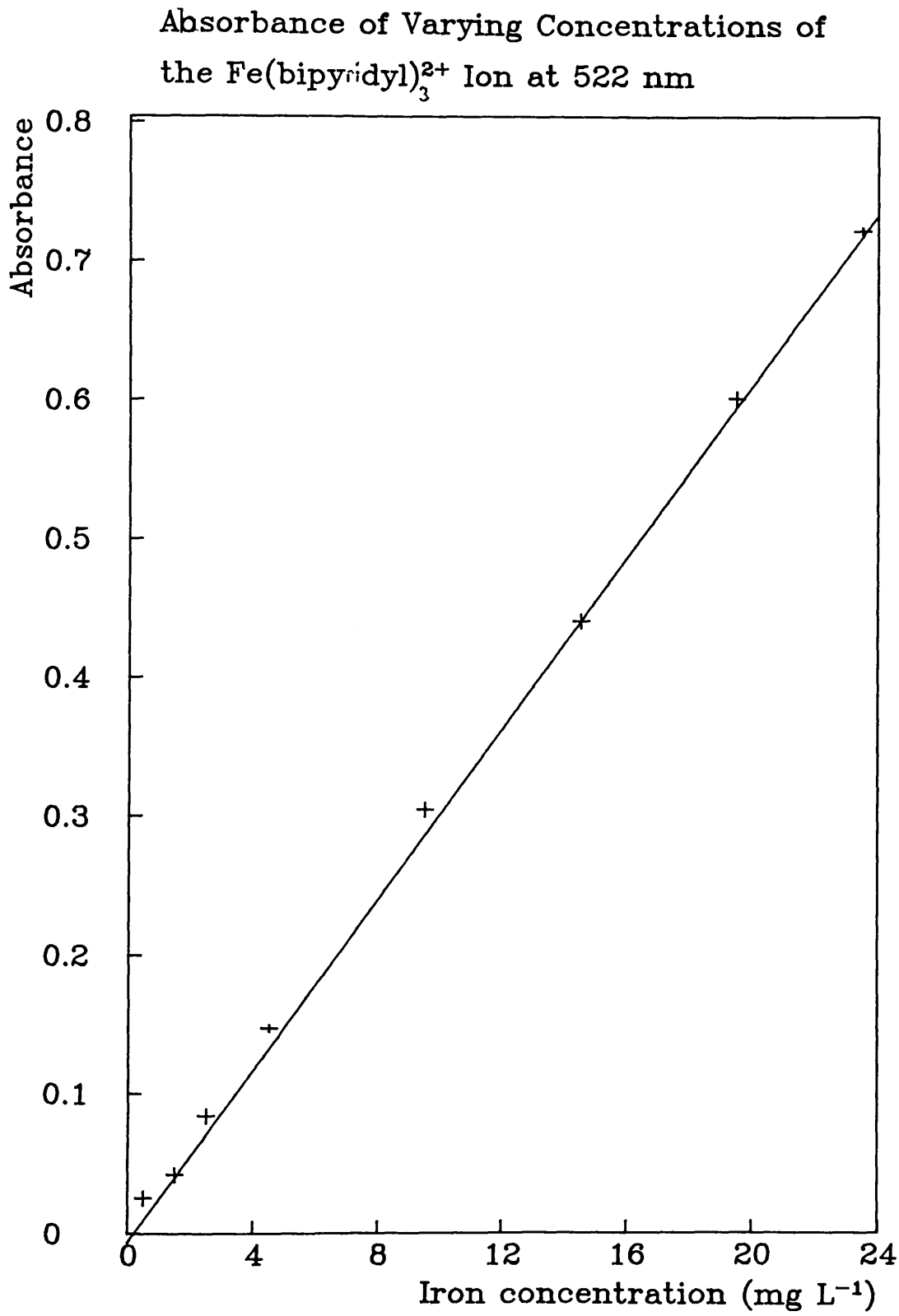

Absorbance of Varying Concentrations of
the Fe(bipyridyl)$_3^{2+}$ Ion at 522 nm
Absorbance
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
4
8
12
16
20
24
Iron concentration (mg L^{-1})

Figure 2.VII

solid distillate obtained was then colourless.

2.4.2. PURIFICATION OF ACETONITRILE.

Acetonitrile was purified to remove traces of acrylonitrile and any other impurities. Two methods were used.

METHOD A.

Reagent grade CH_3CN was refluxed over CaH_2 for several hours before being distilled into a flask containing P_2O_5 over which it was also refluxed for several hours. The CH_3CN was distilled into another flask containing fresh P_2O_5 over which it was again refluxed for several hours before being finally refluxed over CaH_2 for 1h. The CH_3CN was stored over activated molecular sieves (Type 4A) in an inert atmosphere box.

METHOD B.

Reagent grade CH_3CN was refluxed over anhydrous $CuCl_2$ for several hours before being distilled into a flask containing P_2O_5 over which it was refluxed for several hours. The CH_3CN was then distilled into another flask containing fresh P_2O_5 over which it was again refluxed for several hours before being stored over activated molecular sieves (Type 4A) in an inert atmosphere box.

Both these methods produced pure CH_3CN as shown by their electronic spectra (Figure 2.VIII) which has a cut-off point below 200 nm.[59]

Electronic Spectrum of CH_3CN

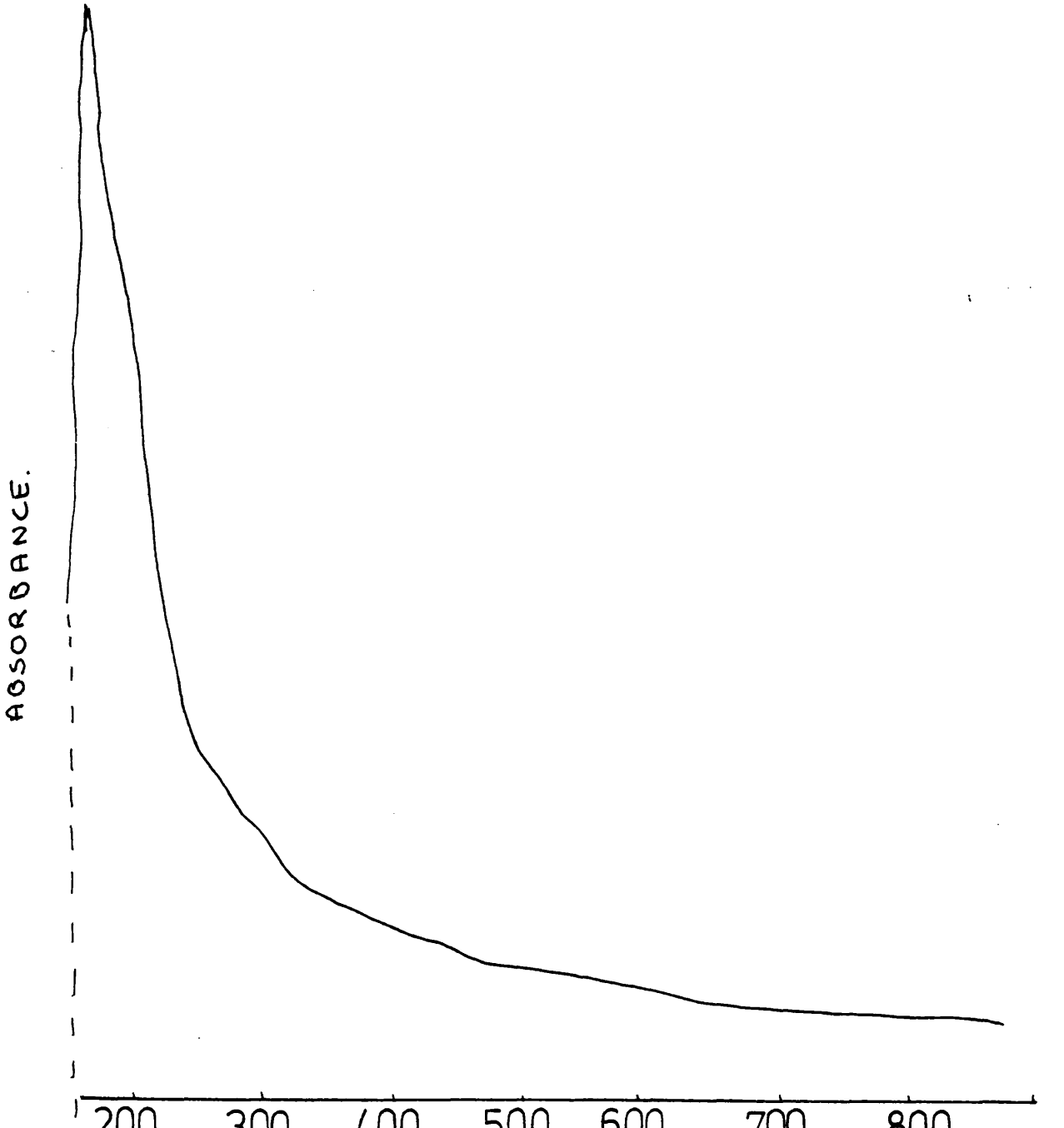


Figure 2VIII

2.4.3. PURIFICATION OF 1,1,1,-TRICHLOROETHANE.

Two types of CH_3CCl_3 were used. These were a) Hopkin and Williams Analar 1,1,1-trichloroethane and b) the commercial solvent Genklene N. They were both purified by distilling the solvent within its boiling range.

The purity of these solvents was checked by examining their gas chromotographic (GC) traces. Solvent (a) was pure and showed only the presence of the solvent peak. (Figure 2.IX) Solvent (b), however, contained some components which had not been removed by distillation. (Figure 2.X) These components were stabilizers which are deliberately added to Genklene during the manufacturing process.

2.5. DETERMINATION OF SPECIFIC ACTIVITY BY GEIGER-MÜLLER (G.M.) COUNTERS.

36-Chlorine is a beta-emitter (β^-) with a half-life of 3×10^5 years. In this type of decay, negative electrons are emitted and the atomic number is increased by one unit. As the half-life of this isotope is so long, no correction to the observed count was needed as the activity would be constant over the period of counting.

Radioactive chlorine was counted in the solid state as $Ag^{36}Cl$ and in the gaseous state as $H^{36}Cl$ and $^{36}Cl_2$ using a Geiger-Müller counter. In its normal form a Geiger-Müller tube consists of an earthed cylindrical case containing a gas. Along the axis of the counter a

GC Trace of 1,1,1-Trichloroethane

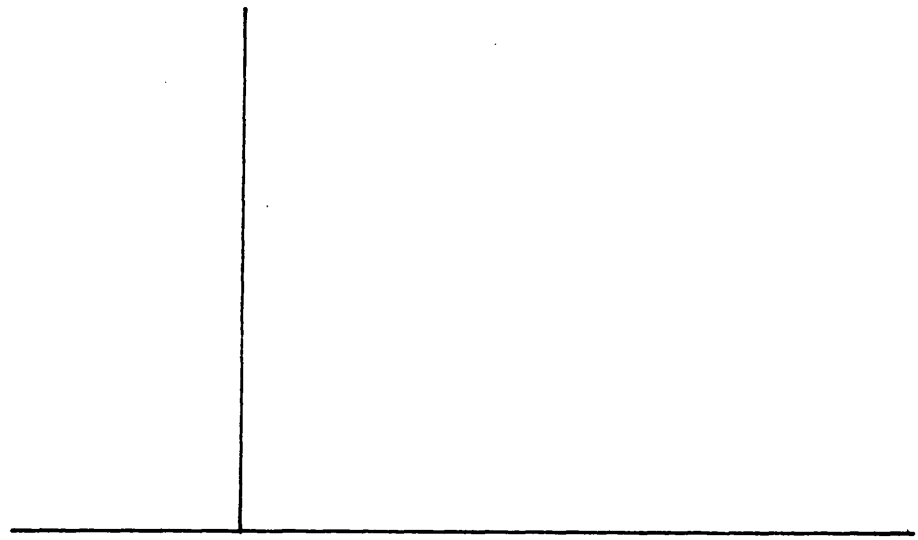


Figure 2IX

GC Trace of Genklene N

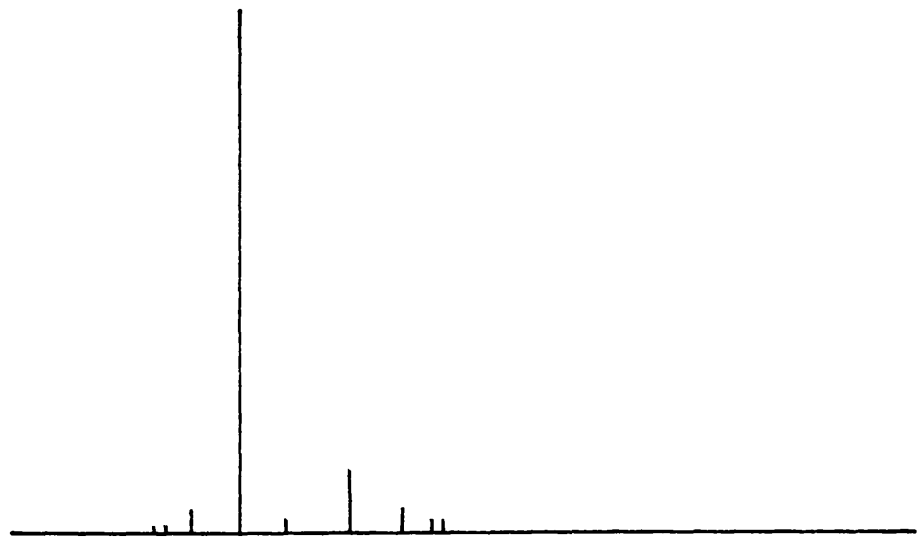


Figure 2X

positively charged electrode is suspended. Ionising radiation incident on the window of the counter, produces an electrical pulse which is amplified in order that it may be recorded. An electronic scaler records the pulses from the counter and produces an output which is proportional to the strength of the initial ionising radiation.

2.5.1. PLATEAU CURVE

In a G.M. counter no counts are recorded until the applied potential is large enough to attract the free electrons to the anode. As the applied potential is increased above this minimum value, Vo, the counting rate increases sharply, until a plateau is reached.

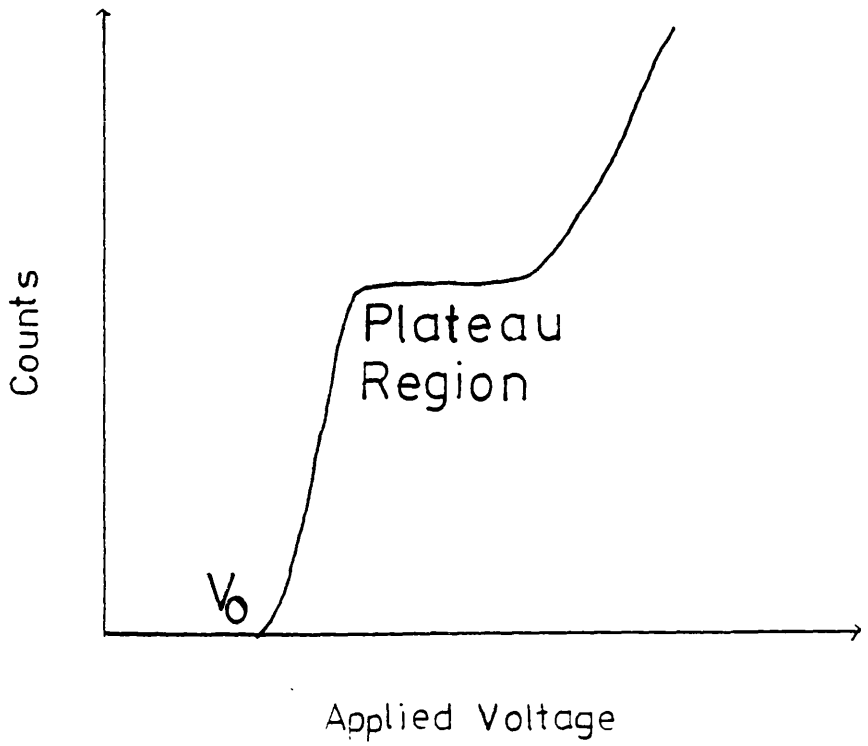


Figure 2XI

The plateau is never flat due to the generation inside the counter of spurious discharges which are not directly initiated by the arrival of particles. These, however, can be quenched by the presence of some alcohol vapour in the counter. As the potential increases, the quencher gas cannot cope with the large number of spurious discharges and the counter begins to discharge.

Plateau regions were determined regularly for every Geiger-Müller tube used by sweeping through the voltage region whilst monitoring the count obtained from a 137-Caesium source. Figure 2.XII shows a typical plateau curve obtained. The working voltage was set in the middle of the plateau region.

2.5.2. DEAD TIME

Immediately after the collection of electrons in a G.M. tube discharge, positive ions are still left in the counter and most of them are very near the centre wire. These positive ions form a space charge which limits the electric field near the centre wire.

If a second particle passes through the counter whilst the positive ions are in this region, an electron avalanche is unable to form, owing to the reduced field near the centre wire. The pulse size which a counter is able to deliver is reduced whilst there are positive ions in the counter. Each pulse from the GM tube is thus followed by a period during which no particles can be detected. This lasts until the positive ions have moved far enough from the centre wire to allow an output

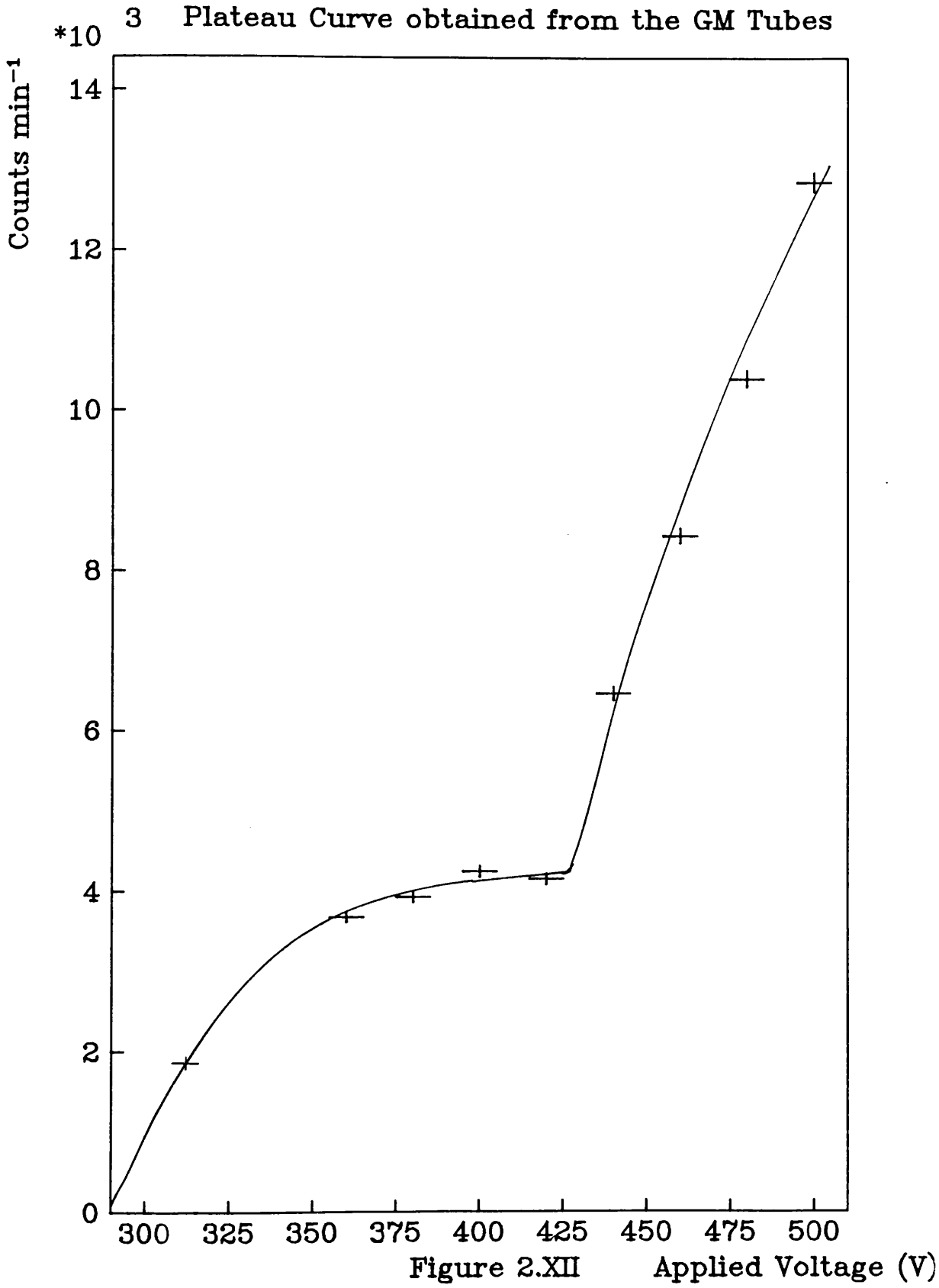

3 Plateau Curve obtained from the GM Tubes
*10
Counts min^{-1}
14
12
10
8
6
4
2
0
300
325
350
375
400
425
450
475
500
Applied Voltage (V)

Figure 2.XII

pulse large enough to operate the recording equipment. This insensitive period is known as the dead time of the counter, and in accurate counting experiments a correction is necessary for counts lost in such periods, especially if the counting rate is high.

It was, therefore, necessary to make dead time corrections on all the counts observed. The G.M. tube used had a dead time of 120 μs but the scalar had a dead time set at 300 μs to give the counter time to recover. The dead time of the scaler was used in all calculations. The true count rate (Nt) was related to the observed count rate No by the relation

$$N_t = \frac{N_o}{(1 - N_o\tau)}$$

where τ is the dead time.

2.5.3. BACKGROUND.

The counter will register some counts in the absence of any source. These counts are due partly to cosmic radiation and partly to γ-radiation from the earth or from traces of radioactive materials in the walls of the room.

The background of a G.M. counter can be reduced by enclosing the counter and source in a container often called a castle. Castles are usually made of lead as this lessens the contribution of any stray radiation. The castle provides the added advantage of allowing an

active sample to be placed at the same distance and position from the counter each time. As scattering of β-particles increases with the atomic number of the scatterer, it is necessary to ensure that the inside of the castle is lined with a material of low atomic weight. For the same reason, the supports of the counter and source must be made of these materials.

The castle was only used for solid $Ag^{36}Cl$. $^{36}Cl_2$ and $H^{36}Cl$ were counted in a glass reaction vessel and thus had a higher background count.

2.5.4. SELF-ABSORPTION.

As 36-chlorine is a β-emitter care was taken to ensure that the GM counters were always the same distance from the sample because of the absorption of β-radiation. This was important when gaseous $^{36}Cl_2$ and $H^{36}Cl$ were counted.

When counting solid $Ag^{36}Cl$, however, a correction for the absorption of β-particles within the solid itself must be made unless the same weight of material is used in all comparative measurements. This is done by measuring apparent β-activity obtained from different thicknesses of samples of identical specific activity. These measurements were obtained for $Ag^{36}Cl$ and a graph, called a self-absorption curve, constructed by plotting the log of activity per mg. against the weight of $Ag^{36}Cl$. The graph obtained using three separate batches of $Ag^{36}Cl$ is shown in Figure 2.XIII. The absorption correction

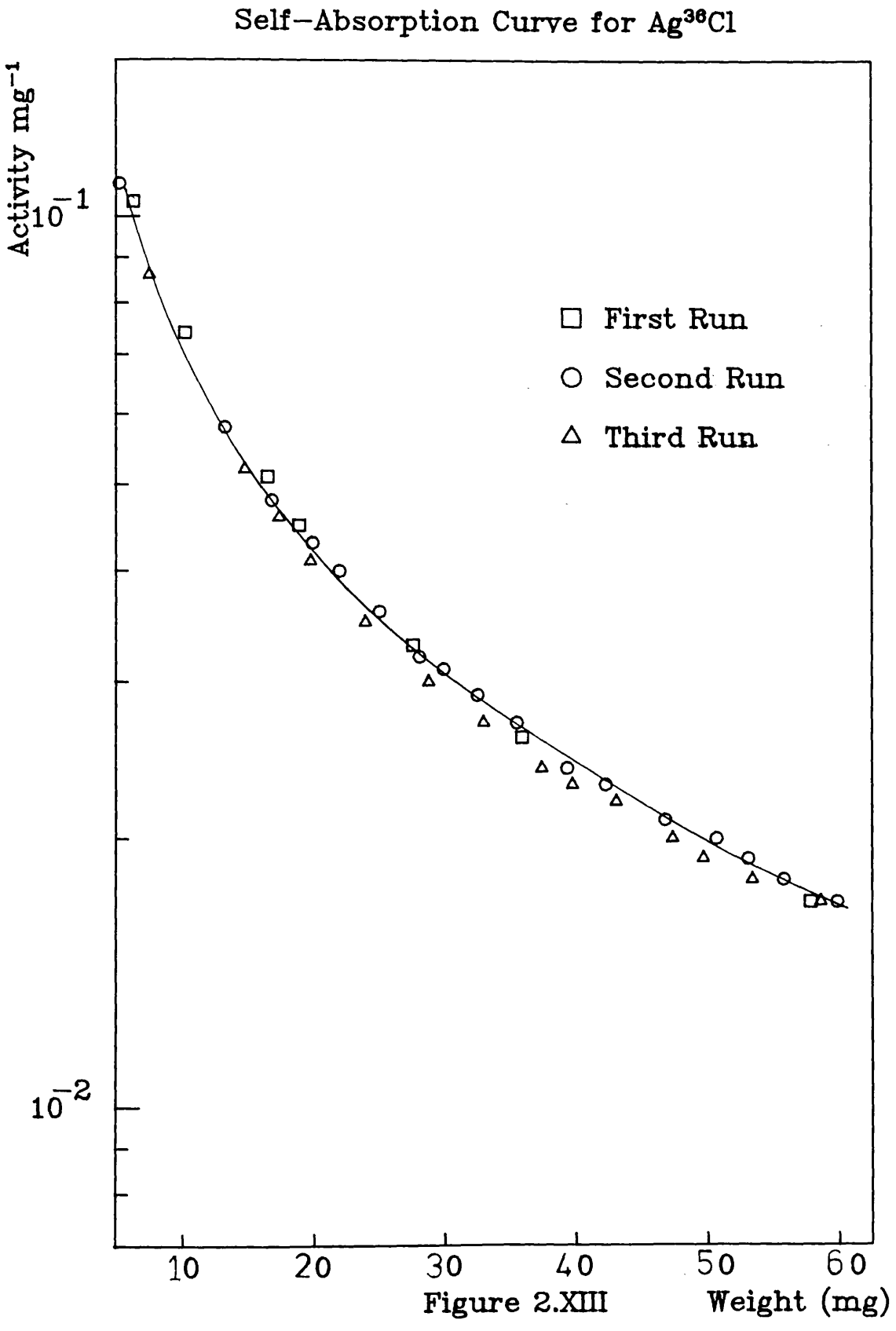


Figure 2.XIII

necessary to relate observations at one thickness to observations at any other thickness within the experimentally determined range is equal to the quotient of the values of log of activity/mg at the two weights.

In all calculations, the activity was related to a weight of 15mg.

In all counts, therefore, corrections were made for background, dead time and self-absorption. (Table 2.III)

CORRECTIONS MADE TO OBSERVED COUNT

Sample	Amount Counted mg.	Counts $600sec^{-1}$	- Background Counts $(600sec)^{-1}$	Corrected For Dead Time Counts $(600sec)^{-1}$	Counts/ mg^{-1} Counts $(600sec)^{-1}$ mg^{-1}	Corrected for Self-Absorption Counts $(600sec)^{-1}$ mg^{-1}
$Ag^{36}Cl$	23.7	14327	14493	14599	616	892

TABLE 2.III

2.5.5. STATISTICAL ERRORS.

All random processes including radioactive decay are subject to fluctuations in measurements due to the statistical nature of the process. Thus even if a source of constant activity is measured under conditions which exclude all errors in measurement, the number of disintegrations observed in successive periods of fixed duration will not be constant.

The distribution of events in a truly random process

such as radioactive decay can be described by a Poisson distribution.

To check that a Poisson distribution was obtained from the counting system, a ^{137}Cs source was used to give 50 readings of 1 minute duration and the total count from each reading, uncorrected for background was used to obtain the distribution shown in Figure 2.XIV. In a Poisson distribution, the square root of the average value, $x^{-\frac{1}{2}}$, is equal to the standard deviation (Equation 2.V)

$$x^{-\frac{1}{2}} = +(\frac{1}{n}\Sigma\sigma) \qquad \ldots\ldots \qquad \text{Eq. 2V.}$$

This relationship was found to hold for the observed distribution. The statistics of all GM tubes used were checked periodically.

All errors quoted on specific activities are the combined errors from the uncertainty in the weight of a sample and from the uncertainty in the count obtained.

2.6. EXCHANGE REACTIONS.

The exchange reactions were monitored by two techniques. Method A enabled the system to be continuously monitored over a short time interval without affecting the stoichiometry. It could, however, only be used to monitor a reaction for approximately 12h as the GM tubes were attacked, when exposed to $^{36}Cl_2$ and $H^{36}Cl$ for longer periods, causing them to continuously discharge. Method B was more suitable for reactions where $FeCl_3$ was dissolved in a solvent and could also be used to follow reactions over

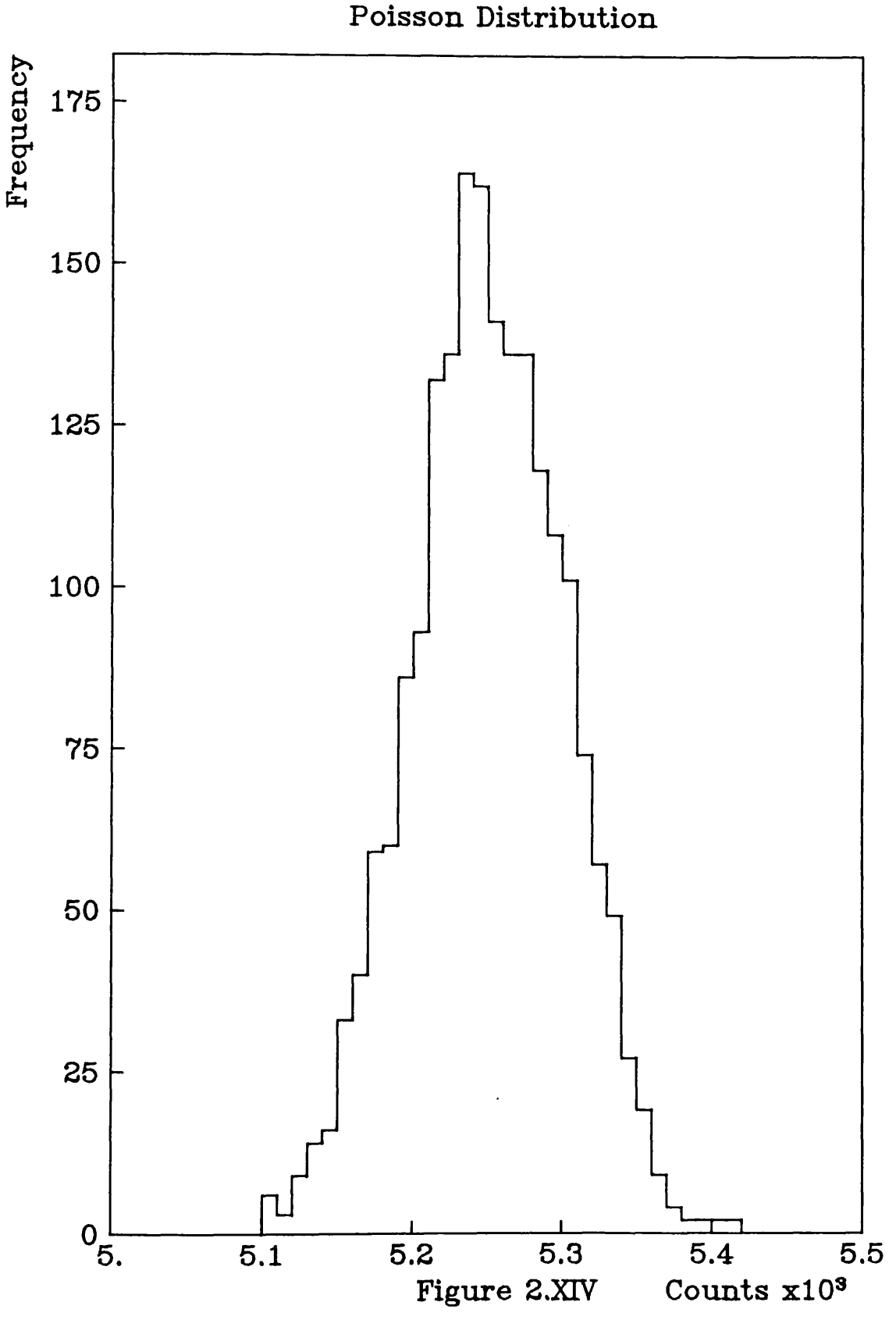

Poisson Distribution
Frequency
175
150
125
100
75
50
25
0
5.
5.1
5.2
5.3
5.4
5.5
Counts x10³

Figure 2.XIV

several days.

2.6.1. EXCHANGE METHOD A.

This method used the apparatus shown in Figure 2.XV which consisted of two G.M. tubes contained in an evacuated glass vessel. Care was taken to ensure that both G.M. tubes were at the same height so that the geometry presented to each was identical. A movable boat enabled any solid sample to be placed directly under one of the G.M. tubes. It was important to make certain that only the G.M. tube with an active solid beneath it registered the activity from that solid. This was tested by placing 137-Caesium directly under one G.M. tube and monitoring the counts from both tubes. (Table 2.IV) The tube with 137-Caesium directly beneath it gave a large count, whereas the other tube gave only a background count.

COUNTS MONITORED BY EACH G.M. TUBE FROM THE SOLID PHASE.

	TUBE 1 COUNTS MIN^{-1}	TUBE 2 COUNTS MIN^{-1}
BACKGROUND	74	65
^{137}Cs. under 1	7210	71
^{137}Cs under 1	6989	63
^{137}Cs under 2	72	6298
^{137}Cs under 2	81	6273

TABLE 2.IV

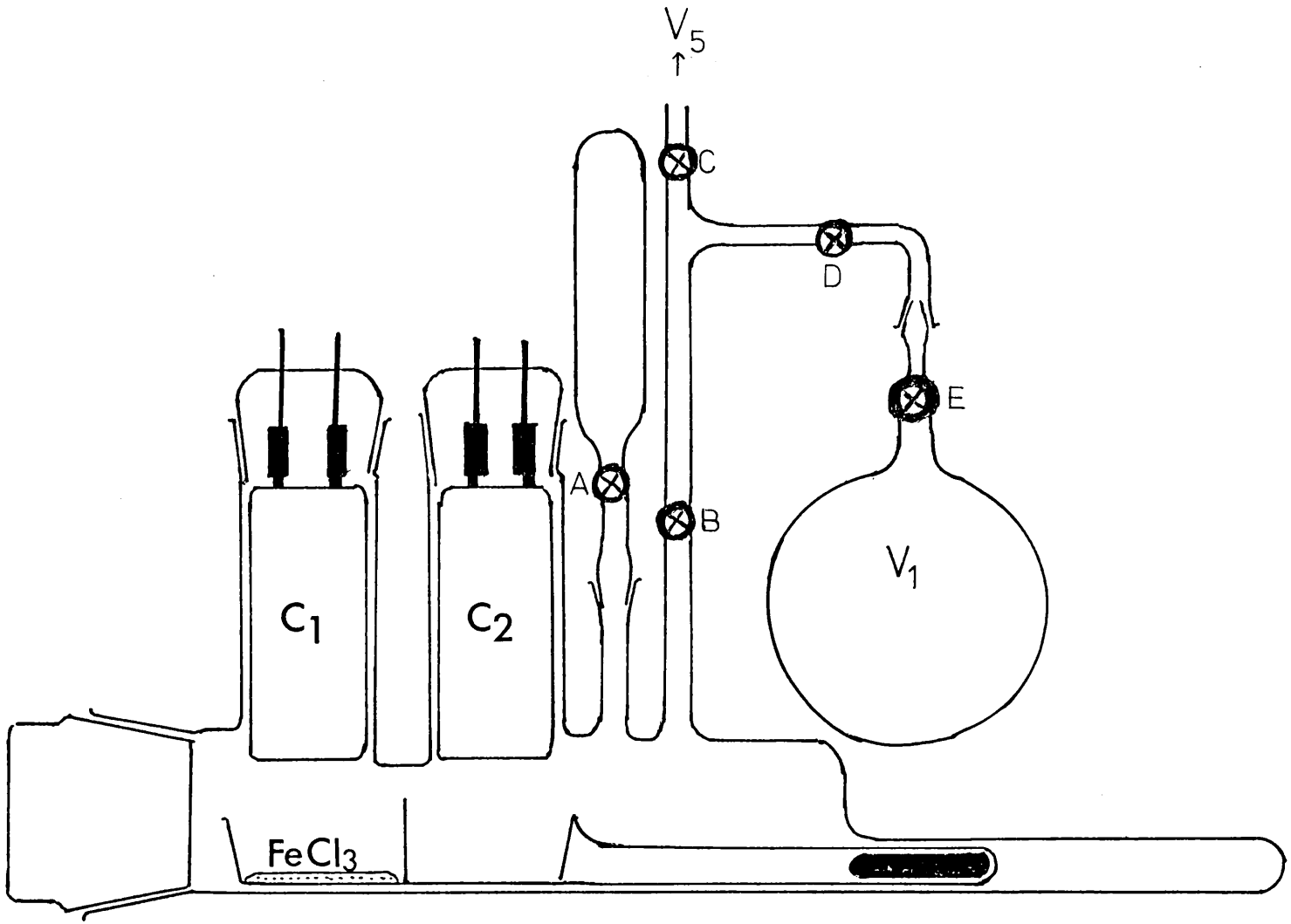


Figure 2XV

Before every exchange reaction, it was necessary to determine the plateau region of both GM tubes and to monitor the background count. As counting characteristics vary slightly, the two tubes were intercalibrated by taking counts using varying pressures of radioactive gas. A graph of pressure vs. counts should give a straight line which passes through the origin. A typical set of results is illustrated in Table 2.V. and the graph shown in Figure 2.XVI. When the counts from both tubes

PRESSURE VS. COUNTS.

Pressure of $H^{36}Cl$ Torr	Counts Min^{-1}
11.5 ± 0.02	490 ± 22
44.1 ± 0.09	1519 ± 40
63.3 ± 0.12	2551 ± 50
110.6 ± 0.20	3576 ± 60
118.4 ± 0.23	3902 ± 62

TABLE 2.V

were plotted (Figure 2.XVII) a straight line was obtained whose gradient was equal to the counting ratio between the two GM tubes. This counting ratio should remain constant and was normally in the region of 1.10

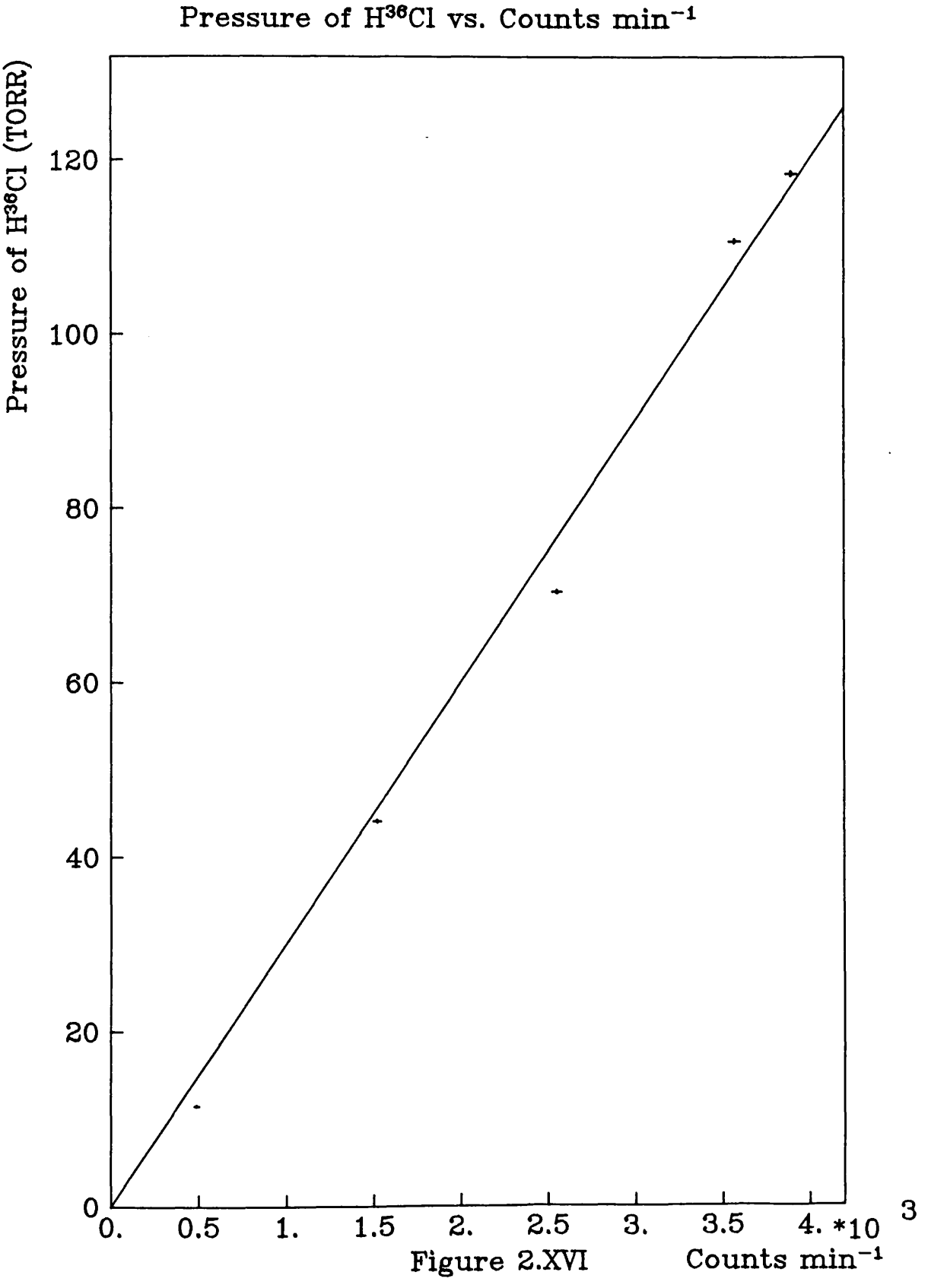

Pressure of $H^{36}Cl$ vs. Counts min^{-1}
Pressure of $H^{36}Cl$ (TORR)
120
100
80
60
40
20
0
0.
0.5
1.
1.5
2.
2.5
3.
3.5
4. *10 3
Counts min^{-1}

Figure 2.XVI

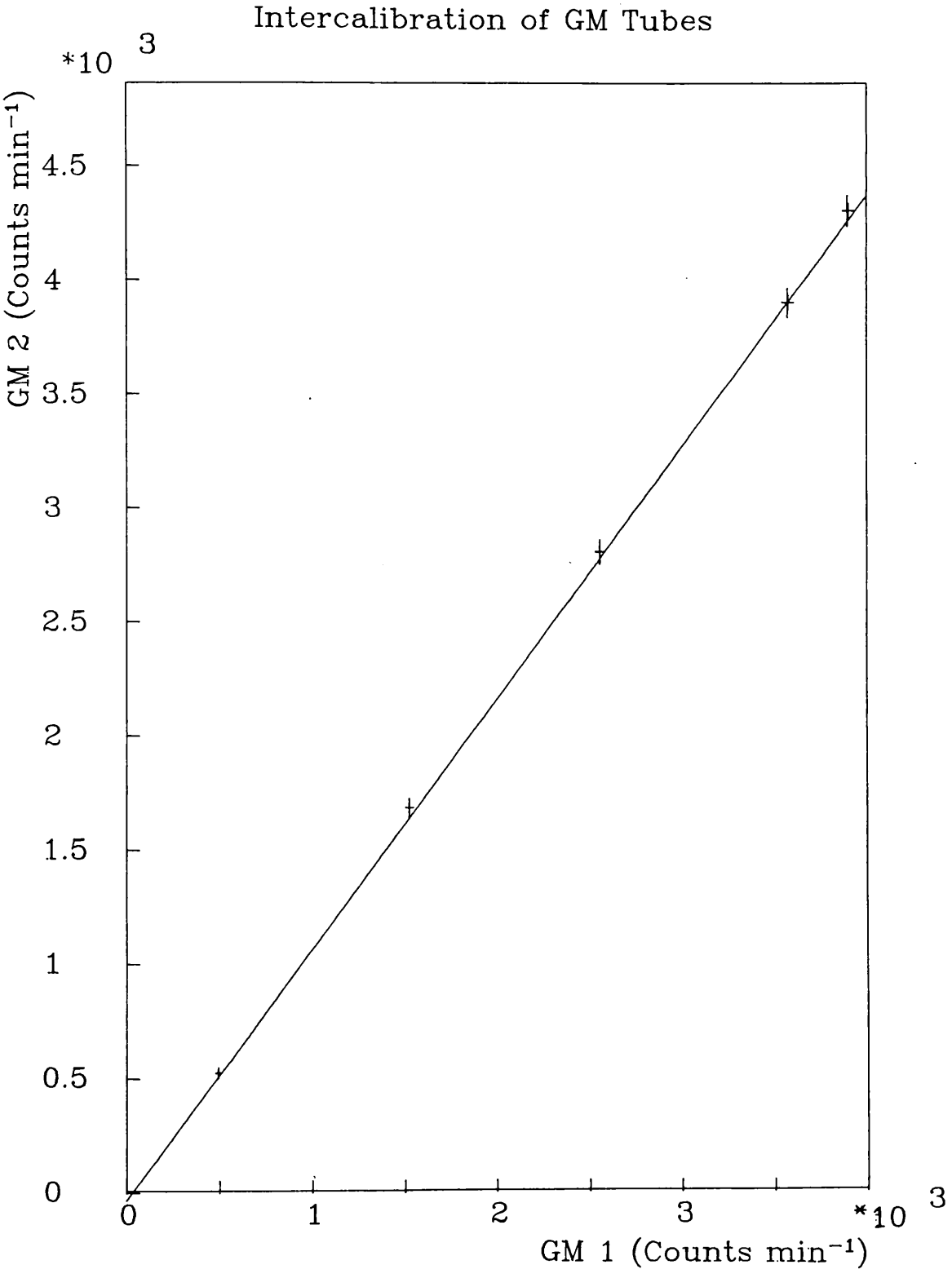


Figure 2.XVII

In an exchange reaction, iron(III) chloride was weighed in an inert atmosphere box and placed in a rotaflo vessel which had previously been flamed and pumped out. It was transferred to a vacuum line where the $FeCl_3$ flask was evacuated before it was joined to the counting vessel containing the two G.M. tubes. (Figure 2.XV) The system was pumped for several hours before the flask was opened and the $FeCl_3$ allowed to fall into the movable boat, which was placed directly under one of the GM tubes.

Vessel V_1 contained a weighed amount of $^{36}Cl_2$ or $H^{36}Cl$ which was admitted to the counting vessel. The GM tube which had the $FeCl_3$ beneath it gave a count due to both the solid and gas whilst the other tube gave a count due only to the gas. The reaction was followed by monitoring the counts from both tubes over a period of time. At the end of the reaction the gas was removed and analysed as outlined in 2.3.1. and the $FeCl_3$ analysed as outlined in 2.3.2.

2.6.2. EXCHANGE METHOD B.

This method used the vessel shown in Figure 2.XVIII which consists of two bulbs of accurately known volume and the ratio was such that $V_1 >> V_2$ (V_1 = 350.1ml, V_2 = 10.5ml). The vessel was flamed and pumped out on a vacuum line before being transferred to an inert atmosphere box where a known amount of $FeCl_3$, either as the solid or in solution, was added to V_1. The vessel was removed, attached to a vacuum line and evacuated. A known pressure of radioactive gas was added and the vessel stored in a thermostat bath at 298K. At intervals radioactive gas was removed by allowing gas into V_2 and as the ratio of $V_1:V_2$ was known, the amount of gas in V_2 was calculated. This sample of gas was distilled into a NaOH solution at 77K, converted to $Ag^{36}Cl$ and its activity determined. At

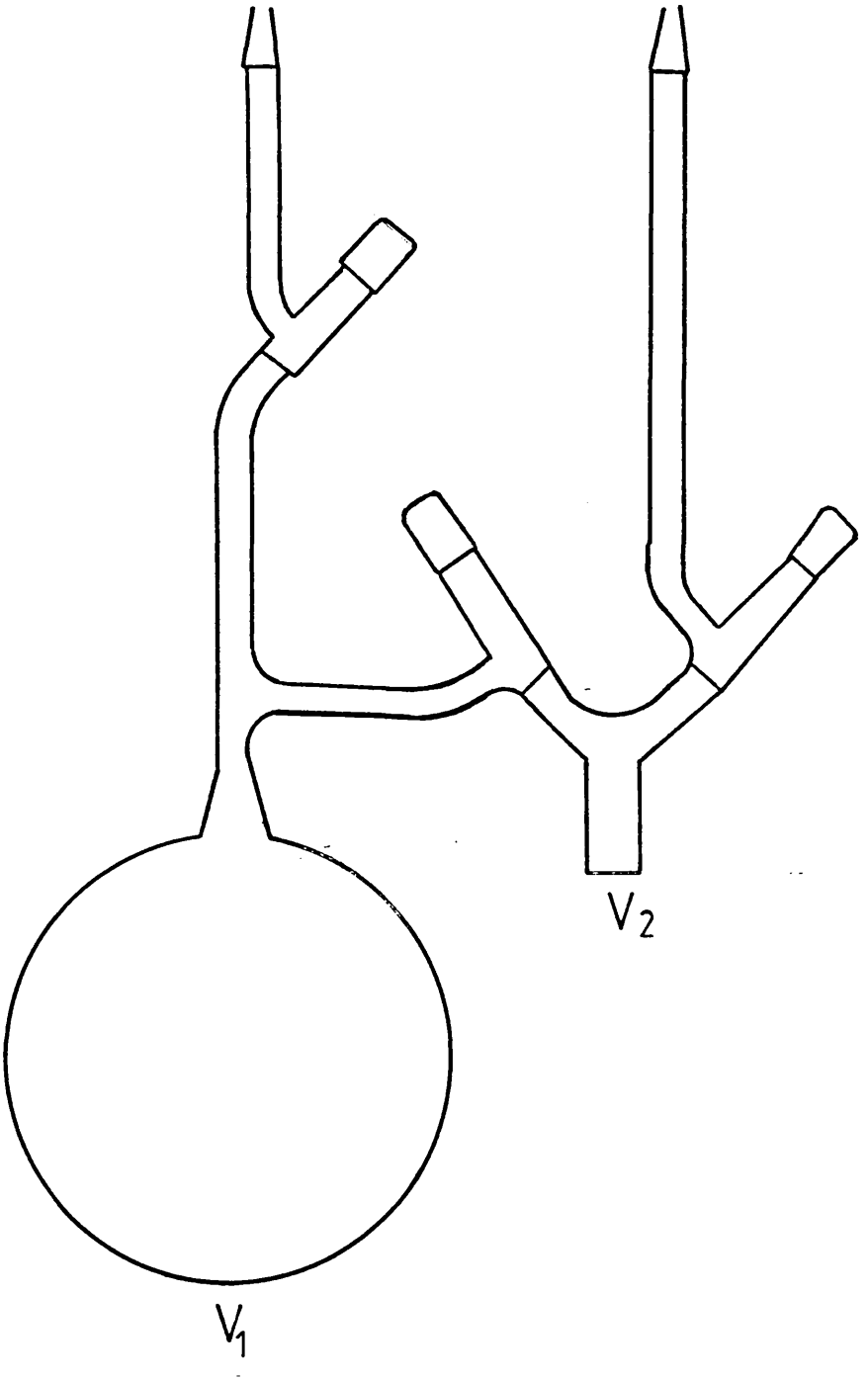


Figure 2XVIII

the end of the reaction, the $FeCl_3$ was hydrolysed and the chloride ion precipitated as silver chloride which allowed any activity incorporated into the sample to be determined.

2.7. GAS-LIQUID CHROMATOGRAPHY.

Gas chromatography is used for the analysis of volatile substances. The substances to be analysed are distributed between two phases, one of which is stationary and the other mobile. In gas-liquid chromatography the column is packed with a porous solid coated with a thin layer of involatile liquid as the stationary phase. Separation is due to differences in solution behaviour. Components of the mixture distribute themselves between the gas phase and the stationary liquid phase according to their partition coefficients. The solid functions only as a support for the liquid stationary phase, enabling it to present a large surface to the gas.

The mobile phase is a gas that is not retained by the stationary phase. Its role is to carry the sample molecules through the chromatographic column and is generally called the carrier gas. At the column outlet there is a detector, which indicates the presence of the compounds emerging at different times in the carrier gas. A flame ionisation detector was used in this work. This operates by burning hydrogen gas in a small metal jet. The jet forms one electrode of the cell and the other, which may be a piece of brass or platinum wire, is mounted at some point near the tip of the flame. The potential difference across the electrodes is about 200V. Pure hydrogen or a hydrogen/carrier gas mixture gives rise to a small background signal which may be offset electrically. A signal is recorded when a substance is ionised in the flame.

The separation of components can be controlled by altering both the flow of the carrier gas and the

temperature of the column. Conditions are selected which give rise to good separation of the components to be analysed.

To determine quantitatively the amount of a component in a solvent it is necessary to construct a calibration curve. This is done by mixing known concentrations of the component in the solvent and measuring the peak heights caused by the component. The amount of sample injected into a column is generally very small and, therefore, any discrepancy in the injection size affects the peak height of the component. To overcome this, a known amount of an internal standard (IS) is mixed with the sample. The peak height ratio of the component and the IS is plotted against the concentration of the component in the solution. Thus if the injection size was slightly low, the size of the component peak and the IS peak would be smaller but the peak height ratio would be the same.

Gas-liquid chromatography (GLC) was used for the quantitative analysis of mono- and tri-chloroacetonitrile in acetonitrile and of vinylidene chloride in 1,1,1-trichloroethane.

2.8. SURFACE AREA DETERMINATION.

The surface areas of the different iron(III) chloride samples prepared were examined using the ^{85}Kr-B.E.T. method.[60.61.] Surface areas are normally measured by determining the amount of gas adsorbed at a given temperature as a function of pressure. When the surface area to

be measured is small, that is below $1m^2$, the change in pressure cannot be measured accurately by conventional techniques. For these small areas 85-Krypton is used as the adsorbate and the small changes in pressure can be accurately determined. This is achieved by calibrating the pressure, determined by a Pirani Gauge, against the activity of the Krypton in counts sec^{-1}, determined by a Geiger-Müller tube. This method makes use of the B.E.T. equation (Equation 2.VI) which relates the gas pressure to the amount of gas adsorbed.

$$\frac{P}{x(P^o-P)} = \frac{1}{x_m C} + \frac{1}{x_m}\frac{P}{P^o} \qquad \text{..... Eq. 2.VI}$$

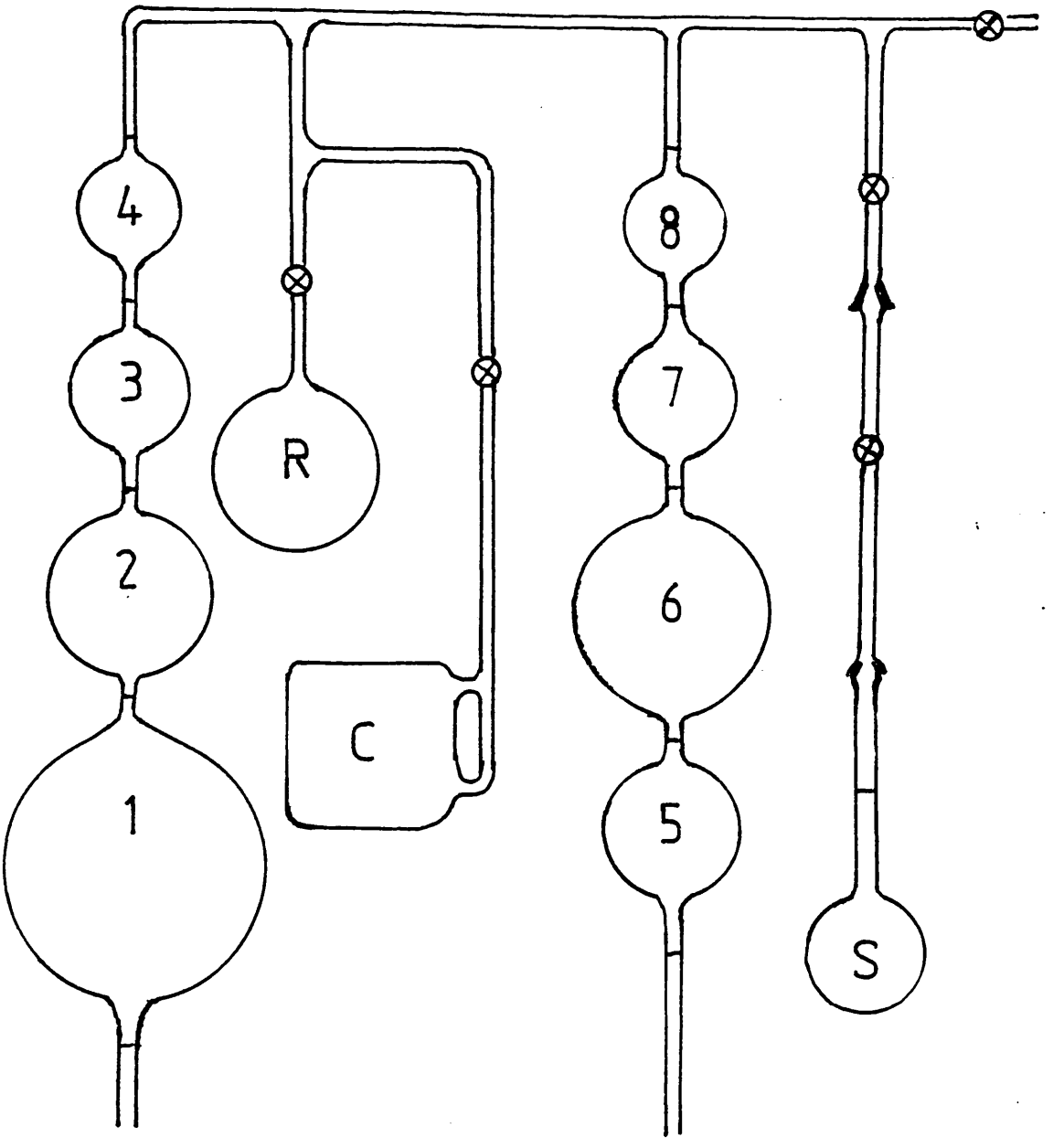
where x = number of molecules adsorbed at pressure P.

P^o = saturated vapour pressure of the gas at the adsorptive temperature. (S.V.P. of Kr at 77K = 0.62 mm Hg)

C = a constant for any particular gas/solid system.

x_m = number of molecules of a gas required to form a monolayer.

The apparatus shown in Figure 2.XIX was a vacuum system which consisted of bulbs of accurately known volume, a counting cell, a Geiger-Müller tube and a storage vessel for the krypton. The volume can be altered by filling the bulbs with mercury and thus changing the pressure, P. For every surface area determination a graph of volume versus Temperature/Pressure was obtained. This gave a straight line which



where vol 1 = 63.07 ml vol 5 = 17.18 ml

vol 2 = 29.53 ml vol 6 = 42.39 ml

vol 3 = 8.79 ml vol 7 = 10.90 ml

vol 4 = 5.19 ml vol 8 = 6.32 ml.

R = ^{85}Kr storage vessel.

C = thin-walled counting vessel.

S = the adsorbent sample bulb.

Figure 2.XIX

intercepted the y-axis at a volume equal to the dead space of the apparatus. The sample being examined was then held at 77K by liquid nitrogen. A correlation was made to take account of the effective volume of the apparatus when part of the system was cooled to 77K (i.e. an increase in effective volume). A straight line of different gradient was obtained when volume versus T/P was plotted. The amount of ^{85}Kr adsorbed was calculated by taking the difference in volume, ΔV, between these two lines. The number of Kr molecules adsorbed (x) is given by Equation 2.VII

$$x = \frac{P\Delta V}{77} \cdot \frac{N}{R} \cdot \frac{1}{760 \times 10^3} \quad \ldots\ldots\ldots \text{Eq. 2VII}$$

where N = Avogadro number (6.02×10^{23} mol l^{-1})

R = gas constant (0.082 l atm mol^{-1} K^{-1})

From the B.E.T. equation it was known that $\frac{P}{x(Po-P)}$ vs $\frac{P}{PO}$ gave a straight line with gradient $\frac{1}{xm}$, where x_m is equal to the number of Kr molecules required to form a monolayer. Thus the surface area was calculated from equation 2.VIII.

$$\text{The surface area} = x_m \cdot \frac{19.5 \times 10^{-20}}{\text{wt. of sample}} \quad m^2 g^{-1} \quad \ldots\ldots \text{Eq. 2VIII}$$

19.5×10^{-20} m^2 is the molecular area of Kr.

CHAPTER THREE

CHAPTER 3

SURFACE AREA DETERMINATION OF IRON(III) CHLORIDE.

As a preliminary to heterogeneous exchange reactions, the surface areas of various iron(III) chloride samples were determined in an attempt to correlate any differences in surface areas with different exchange rates. Three samples of iron(III) chloride were examined and these were:-

Sample A	$FeCl_3$ prepared by the passage of Cl_2 over iron wire, (cf. 2.2.1.A)
Sample B	$FeCl_3$ prepared by $SOCl_2$ dehydration of $FeCl_3.6H_2O$ (cf. 2.2.1.B),
Sample C	Commercial anhydrous $FeCl_3$ (cf. 2.2.1.C).

When a gas is allowed to come into contact with the surface of a solid, the gas may be adsorbed by the surface depending upon the experimental conditions. This adsorption is either chemical or physical in nature depending upon the type of bond formed between the gas molecules, the adsorbate, and the solid surface, the adsorbent. In adsorption, the extent of coverage of the surface is related to the pressure of the adsorbate gas. To determine the surface area of a sample it is necessary to determine when the adsorbed monolayer is complete. This is done using the B.E.T. equation which relates the gas pressure to the amount adsorbed (cf. 2.8. Eq. 2.VI).

The surface areas of the iron(III) chloride samples were determined using the radio-isotope 85-krypton as adsorbate. The advantage of using radioactive gas is that small changes in pressure can be determined relatively rapidly and with a high precision. The apparatus used is described in section 2.8. Since it was necessary to examine these samples under anhydrous conditions, they were prepared in an inert atmosphere box where they were ground to a uniform size using a mortar and pestle. It was not possible to machine-grind these samples as they had to be prepared in an anhydrous atmosphere.

A typical calculation is shown in Table 3.I and Figure 3.I. The number of krypton molecules (x) is given by

$$x = \frac{P\Delta V}{T}.\frac{N}{R}.\frac{1}{760} \times 10^{3}$$

where P = Pressure (mm Hg)

ΔV = Change in volume (ml)

N = Avogadro number (6.022×10^{23} mol^{-1})

T = Temperature at which adsorption isotherm is determined, that is 77K.

R = gas constant (0.082 l at mol^{-1} K^{-1}).

The B.E.T. equation states that

$$\frac{P}{x(P^{o}-P)} = \frac{1}{x_m}\frac{P}{P^{o}} + \frac{1}{x_m C}. \qquad \ldots\ldots \text{Eq. 2.VI.}$$

Therefore, a graph of $\frac{P}{x(P^{o}-P)}$ versus P/P^{o} gives a straight line whose gradient is equal to the reciprocal

SURFACE AREA CALCULATION.

Vol. ml.	Counts $(100sec)^{-1}$	Counts $(100sec)^{-1}$ − Background	Counts $(100sec)^{-1}$ Corrected for Dead Time	Counts $(sec)^{-1}$	P mm Hg.	$\frac{T}{P} \times 10^{3}$	Δv	$x \times 10^{18}$	$P^{o} - P$	$\frac{x(P^{o}-P)}{10^{18}}$	$\frac{P \times 10^{-18}}{x(P^{o}-P)}$	$\frac{P}{P^{o}}$
183.3	4459	4378	4436	44.36	0.049	5.98						
120.4	5828	5747	5848	58.48	0.064	4.56						
76.8	7495	7414	7583	75.83	0.083	3.51						
17.2	12267	12186	12649	126.49	0.142	2.07						
0	14619	14538	15201	152.01	0.171	1.72						
183.3	3486	3405	3440	34.40	0.038	7.72	43	0.204	0.582	0.119	0.320	0.061
120.4	4412	4331	4388	43.88	0.048	6.12	40	0.239	0.572	0.137	0.351	0.077
90.8	5046	4965	5040	50.40	0.055	5.34	39	0.267	0.565	0.151	0.364	0.089
76.8	5371	5290	5375	53.75	0.059	4.98	38	0.280	0.561	0.157	0.376	0.095
59.6	5902	5821	5924	59.24	0.065	4.53	36	0.292	0.555	0.162	0.402	0.105
17.2	7720	7639	7818	78.18	0.086	3.42	34	0.365	0.534	0.195	0.442	0.139
0	8756	8675	8907	89.07	0.099	2.99	33	0.405	0.522	0.212	0.466	0.159

TABLE 3.I.

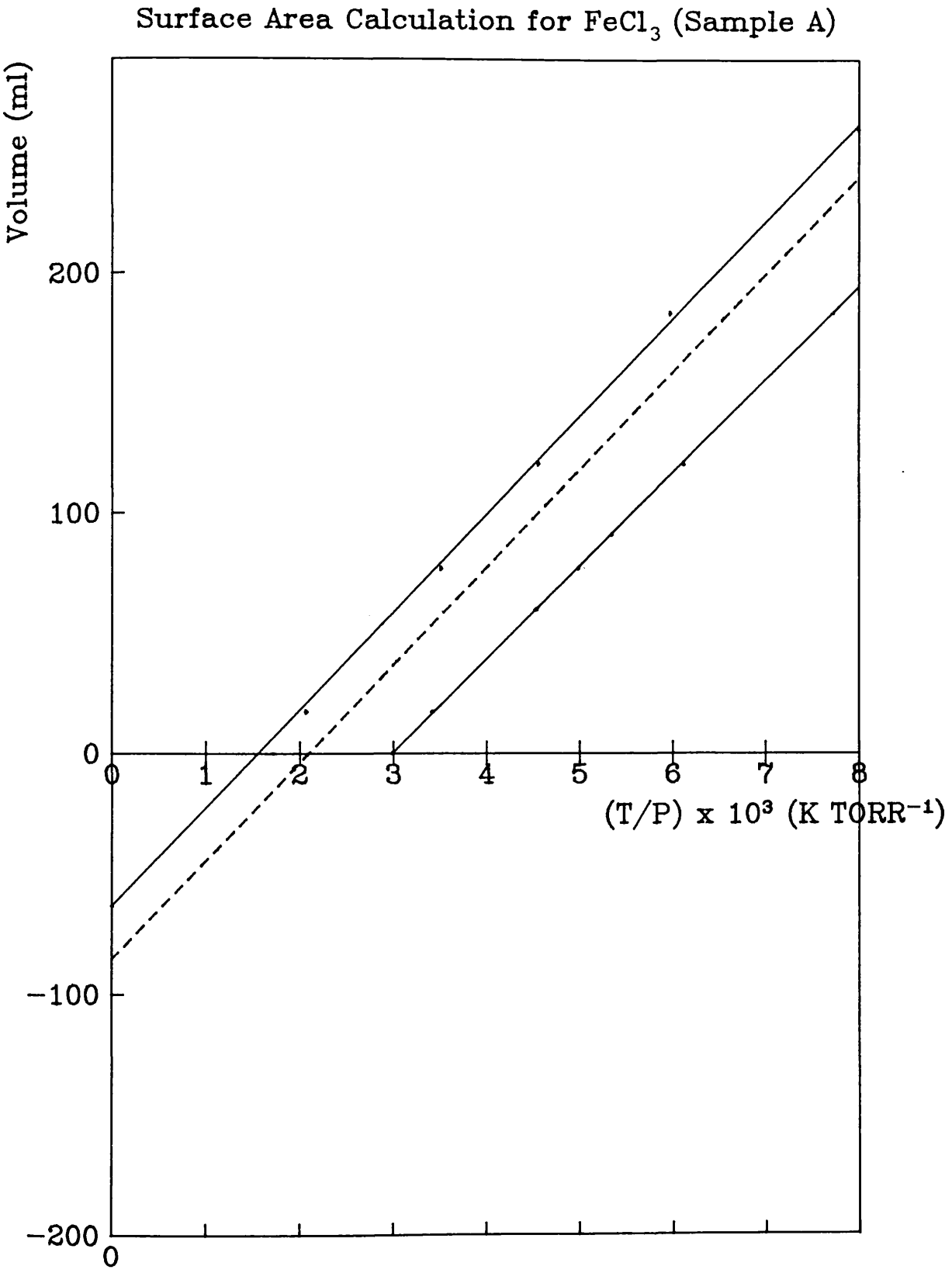

Surface Area Calculation for $FeCl_3$ (Sample A)
Volume (ml)
200
100
0
−100
−200
0
1
2
3
4
5
6
7
8
(T/P) x 10^3 (K TORR^{-1})

Figure 3.I

of the number of Kr molecules required to form a monolayer. (Figure 3.II).

$$\text{Gradient} = \frac{(0.4730 - 0.3525)}{0.16 - 0.08} \times 10^{-18}$$

$$\frac{1}{x_m} = 1.51 \times 10^{-18}$$

$$\rightarrow \quad x_m = 0.66 \times 10^{18}$$

$$\text{The Surface Area} = \frac{x_m \times \text{molecular area of Kr.}}{\text{sample weight}}$$

$$= \frac{0.66 \times 10^{18} \times 19.5 \times 10^{-20}}{0.8941}$$

$$= 0.14 \ m^2 g^{-1}$$

Several results were obtained, using different samples, for each of the three types of iron(III) chloride (Table 3.II). In all cases the surface areas obtained are small and their order of magnitude is such that

Sample A < Sample B < Sample C.

Single crystal and powder pattern X-ray studies performed at room temperature on $FeCl_3$, prepared by the passage of Cl_2 over iron wire, indicate that the chlorine atoms are hexagonally close packed with the iron atoms in a layered array in the interstices of the chlorine lattice. The sequence of atom planes is Cl, Fe, Cl, Cl, Fe, Cl, etc. with two-thirds of the possible Fe

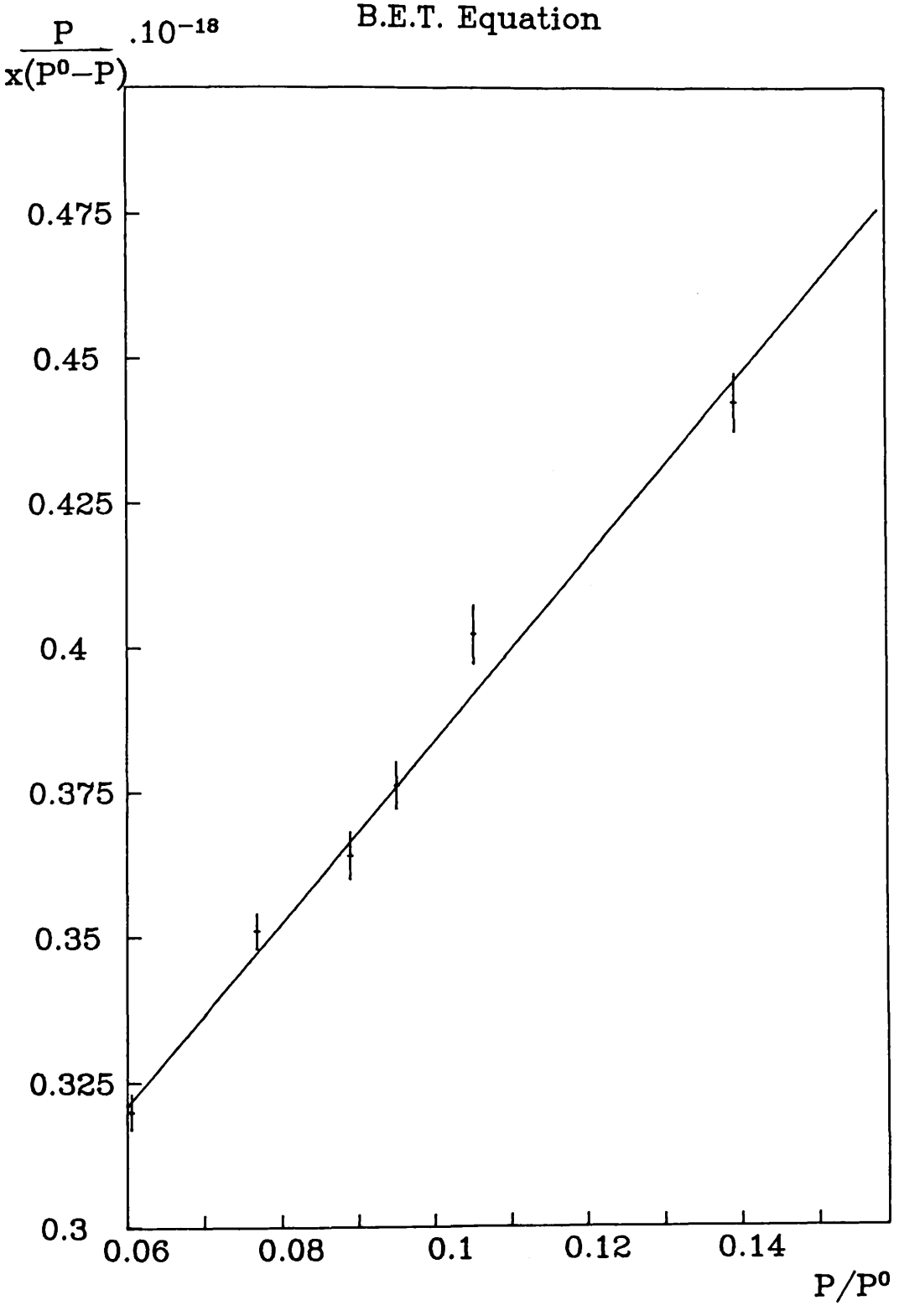
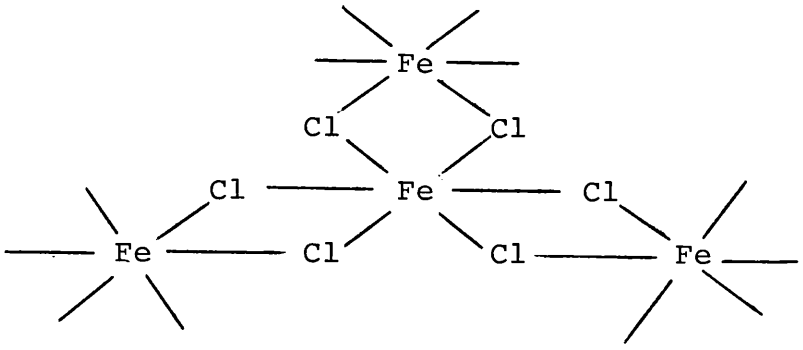

B.E.T. Equation
P / x(P⁰−P) .10⁻¹⁸
0.475
0.45
0.425
0.4
0.375
0.35
0.325
0.3
0.06
0.08
0.1
0.12
0.14
P/P⁰

Figure 3.II

sites occupied. The iron atoms are in sites of approximately octahedral symmetry.[11]. (Formula 3.I).



Formula 3.I

The X-ray powder pattern of $FeCl_3$ prepared by thionyl chloride dehydration of $FeCl_3.6H_2O$ indicates that stacking faults exist in its structure.[62]. This will cause the surface to be less regular and result in sample B having a larger surface area than sample A. Sample C is made commercially on a large scale and is not expected to be as pure as sample A. The presence of impurities would lead to sample C having a larger surface area.

SURFACE AREAS OF IRON(III) CHLORIDE SAMPLES

	Surface Areas. $m^2 g^{-1}$
SAMPLE A	0.14 ± 0.02 0.15 ± 0.02 0.15 ± 0.02
SAMPLE B	0.20 ± 0.02 0.23 ± 0.02 0.22 ± 0.02
SAMPLE C	0.34 ± 0.02 0.36 ± 0.02 0.37 ± 0.02

TABLE 3.II.

CHAPTER FOUR

CHAPTER 4

INTERACTION OF IRON(III) CHLORIDE WITH CHLORINE

In the presence of molecular chlorine, iron(III) chloride can function as a chlorination catalyst, though it is also possible for $FeCl_3$ to chlorinate hydrocarbons non-catalytically in the absence of chlorine. The catalytic ability of iron(III) chloride is well established though the reasons for this are not completely understood. To investigate the role of $FeCl_3$ as a catalyst and especially the Fe(III)-Cl bond lability in situations relevant to catalysis, exchange reactions were performed between $FeCl_3$ and 36-chlorine. In the preparation of chlorinated hydrocarbons, $FeCl_3$ is sparingly soluble in many reaction mixtures and a donor solvent is often used to dissolve the $FeCl_3$. Exchange reactions were, therefore, performed under homogeneous conditions by dissolving $FeCl_3$ in acetonitrile. In the homogeneous medium, the chemical effects of dissolving $FeCl_3$ in acetonitrile have been fully investigated using electronic spectroscopy, Fe^{II} and Fe^{III} analysis and gas chromatography.

4.1. EXCHANGE REACTIONS.

Exchange reactions occur when atoms of a given element interchange between two different chemical states. Exchange can be observed by labelling one of the elements with a radioisotope and following the position of the isotope.[63.] (4I)

$$AB^{*} + BC \rightleftharpoons AB^{*} + \overset{*}{B}C \qquad \text{.....(4I).}$$

At first only the heavy elements with naturally occurring radioactive isotopes could be used to follow exchange reactions. Artificial radioactivity was discovered in 1934 when aluminium foil which had been bombarded with α-particles gave off radiation after the bombardment had ceased (4II) and this led to the availability of radioisotopes of the lighter elements.[64]

$$^{27}_{13}Al + {}^{4}_{2}He \longrightarrow {}^{30}_{15}P + {}^{1}_{0}N \qquad \text{.....(4II)}$$

Due to the low neutron fluxes available at this time only short-lived isotopes of low specific activity were produced. After 1945, the development of nuclear reactors and particle accelerators enabled the production of both short and long-lived radioisotopes of nearly all elements. This removed most of the restrictions on the systems which could be examined and exchange reactions have provided much information on a wide variety of topics, for example molecular structure, bond types and reaction kinetics.[65.66.] They are also very useful in investigating phenomena relating to catalysis. The sensitivity of detection of radioactivity makes it of considerable value in the study of surface processes.[67.]

Exchange reactions follow a first-order rate law regardless of the number of atomic species which participate, since there can be no change in the concentration of the reactants.[68]. It is possible, therefore, to carry out quantitative investigations of exchange reactions. Results can be expressed by the fraction of activity exchanged (f) which has occurred, where f is defined by equation I.[69.70].

$$f = \frac{\frac{xA_1}{xA_1 + yA_2}}{\frac{xM_1}{xM_1 + yM_2}} \qquad \text{.....(Eq. 4.I)}$$

where A = activity in count min^{-1}

M = number of mmol.

x,y = number of exchangeable atoms in species

1,2 = exchangeable species (species 1 has no radioactivity initially).

The value obtained for f indicates the degree to which exchange has occurred (Table 4.I) between two species, one of which was originally inactive.

EXPLANATION OF f-VALUES

f-value	
0	No exchange
0 → 1	Partial exchange
1	Complete exchange
>1	Adsorption or exchange & adsorption

TABLE 4.I.

Obviously when no exchange takes place, f will be 0. If complete exchange occurs and the label is randomly distributed between the two different chemical states then f will equal 1. A value greater than 1 means that more activity is present in the species, which was originally inactive, than can be accounted for solely by exchange and is indicative of adsorbtion of the active species by the inactive species or isotopic fractionation.

4.1.1. CHOICE OF ISOTOPE.

In general the choice of isotope is determined by three factors. These are

a) the availability of the isotope,

b) the length of its half-life,

c) the ease of detection.

In this study, exchange reactions were used to investigate Fe(III)-Cl bond lability in situations relevant to catalysis. Thus a radioisotope of chlorine was used in the exchange reactions. The most common isotopes of chlorine are shown in Table 4.II.

ISOTOPES OF CHLORINE

Isotope	% Abundance	Half Life	Principal Mode of Decay (Energy MeV).
^{35}Cl	75.53	Stable	-
^{36}Cl	-	3.0×10^5 y.	β^- (0.714)
^{37}Cl	24.47	Stable	-
^{38}Cl	-	37.3 m.	β^-(4.81,1.11,2.77)

TABLE 4.II

The 36-chlorine isotope is the most suitable owing to the length of its half-life.

4.2. EXPERIMENTAL.

Exchange reactions were carried out between iron(III) chloride and $^{36}Cl_2$ under both homogeneous and heterogeneous conditions. In the latter case, three different types of $FeCl_3$ were investigated in an attempt to relate exchange behaviour with the mode of preparation and the surface area of the $FeCl_3$. The three types used were:-

Sample A — $FeCl_3$ prepared by the passage of Cl_2 over iron wire. (cf. 2.2.1.A.)

Sample B — $FeCl_3$ prepared by $SOCl_2$ dehydration of $FeCl_3.6H_2O$. (cf. 2.2.1.B.)

Sample C — Commercial anhydrous $FeCl_3$ (cf. 2.2.1.C.)

4.2.1. ADSORPTION OF $^{36}Cl_2$ BY THE REACTION VESSEL.

This reaction was performed using exchange method A. (cf. 2.6.1.) The flask, V_1, (Figure 2.XV) was filled with $^{36}Cl_2$, attached to the line and the system pumped overnight. The background reading was obtained from both GM tubes. (TABLE 4.III). A known pressure (34mm) of $^{36}Cl_2$ (equivalent to 0.0654g; 0.92 mmol.), measured by the manometer, was admitted to the reaction vessel. Tap B was closed and the radioactivity monitored over a period of 4.75h. (Table 4.IV). The $^{36}Cl_2$ was removed to volume, V_5. (Figure 2.XV) and the system pumped overnight. This procedure was repeated twice using (0.0596g; 0.84 mmol) and (0.0569g; 0.80 mmol.) of $^{36}Cl_2$ respectively. (Tables 4.V + 4.VI). The background

ADSORPTION OF $^{36}Cl_2$ BY REACTION VESSEL - RUN I.

Counts min^{-1} Tube 1	- Background	Corrected for Dead Time	Counts min^{-1} Tube 2	-Background	Corrected for Dead Time	Time Min.
10399	10006	10533	11159	10307	10867	5
10464	10071	10605	10800	9948	10469	8
10339	9946	10466	10896	10044	10575	10
10139	9746	10245	10658	9806	10312	15
9081	8688	9082	9953	9101	9535	35
9066	8673	9066	9586	8734	9133	50
7261	6868	7112	8060	7208	7478	153
7238	6845	7088	8238	7386	7669	160
6843	6450	6665	7691	6839	7081	180
6434	6041	6229	7605	6753	6989	195
6225	5832	6007	6787	5935	6116	240
5827	5434	5586	6725	5873	6051	270
5717	5324	5470	6644	5792	5965	280
5828	5435	5587	6581	5729	5898	285

TABLE 4.IV

Adsorption of $^{36}Cl_2$ by the Reaction Vessel - Run II.

Counts min^{-1} Tube 1	- Background	Corrected for Dead Time	Counts min^{-1} Tube 2	- Background	Corrected for Dead Time	Time Min
10818	10277	10834	11126	10221	10771	5
10514	9973	10496	10207	9302	9756	10
9444	8903	9318	10071	9166	9606	30
8794	8253	8608	9529	8624	9013	50
8186	7645	7949	9173	8268	8625	120
7681	7140	7404	8765	7860	8182	180
7357	6816	7056	8588	7683	7990	195
7100	6559	6781	8560	7655	7960	240
7104	6563	6786	8246	7341	7621	285

TABLE 4.V

Adsorption of $^{36}Cl_2$ by the Reaction Vessel - Run III

Counts min^{-1} Tube 1	- Background	Corrected for Dead Time	Counts min^{-1} Tube 2	- Background	Corrected for Dead Time	Time Min
11030	10401	10972	11472	10438	11013	5
10919	10290	10848	10983	9949	10470	10
10635	10006	10533	10799	9765	10266	30
10432	9803	10308	10531	9497	9970	50
10437	9808	10314	10248	9214	9659	120
10276	9647	10136	10139	9105	9539	180
9906	9277	9728	10004	8970	9391	195
9741	9112	9547	9956	8922	9339	240
9433	8804	9209	9843	8809	9215	285

TABLE 4.VI

readings after each exposure to $^{36}Cl_2$ are shown in Table 4.III.

BACKGROUND FROM REACTION VESSEL AFTER EXPOSURE TO $^{36}Cl_2$.

	GM.1 Count Min^{-1}	GM.2 Count Min^{-1}
Initial	393 ± 20	852 ± 29
After 1st exposure	541 ± 23	905 ± 30
After 2nd exposure	629 ± 25	1034 ± 32
After 3rd exposure	720 ± 27	1296 ± 36

TABLE 4.III

4.2.2. $FeCl_3$ (sample A) AND $^{36}Cl_2$:- EXCHANGE METHOD A.

Iron(III) chloride (0.9805g; 6.04 mmol.) was placed in a previously flamed-out reaction vessel in an inert atmosphere box. It was transferred to a vacuum line where the $FeCl_3$ flask was evacuated before it was attached to the counting vessel via a ground glass joint. (Figure 2.XV., section 2.6.1.). The system was pumped for several hours before this flask was opened and the $FeCl_3$ allowed to fall into the movable boat. The boat, containing the $FeCl_3$ was placed directly under one of the GM tubes.

A bulb (vol. = 124.6 ml) was evacuated and weighed before the addition of anhydrous $^{36}Cl_2$. The specific

activity of the $^{36}Cl_2$ had been determined and was 233 ± 13 counts min^{-1} mg^{-1}. The bulb was reweighed, attached to the vacuum line at position V_1 and the system pumped overnight. Tap C was closed and $^{36}Cl_2$ admitted to the reaction vessel, which was then isolated from the rest of the system by closing tap B. The amount of $^{36}Cl_2$ in contact with the $FeCl_3$ was calculated as follows.

The initial $^{36}Cl_2$ sample (N_I) = 1.287 mmol.

$\therefore$ $^{36}Cl_2$ in reaction vessel (N_F) = $N_I \frac{V_R}{V_T}$

where V_R = volume of reaction vessel = 498.7 ml

V_T = total volume of system = 650.3 ml. (that is the bulb = 124.6 ml., the reaction vessel = 498.7 ml, the dead space = 27 ml.)

$\therefore$ $N_F = \frac{1.287 \times 498.7}{650.3}$

$= 0.99$ mmol.

After the addition of $^{36}Cl_2$ (0.0701g; 0.99 mmol.) the counts from both tubes were monitored for 22.5 hours (Table 4.VII). The chlorine was removed, precipitated as silver chloride and its specific activity determined. (cf. 2.3.1.)

4.2.3. $FeCl_3$(sample A) AND Cl_2: EXCHANGE METHOD A.

After the removal of $^{36}Cl_2$ from $FeCl_3$ (sample A), a bulb containing a weighed amount of inactive chlorine

RESULTS FROM EXCHANGE METHOD A FOR IRON(III) CHLORIDE (SAMPLE A)

Counts(5min)$^{-1}$ in solid & Gas Phases	± Background	± Corrected for Dead Time	Tubes inter-calibrated	Counts(5min)$^{-1}$ in Gas Phase	± Background	± Corrected for Dead Time	Surface Activity of $FeCl_3$ Counts (5min)$^{-1}$	Time Min.
27834	22194	22698	24060	27417	20855	21299	2761	0
27567	21927	22419	23764	28038	21476	21947	1817	6
27030	21390	21858	23170	27204	20642	21077	2093	10
28053	22413	22927	24301	25389	18827	19188	6201	35
29202	23562	24131	25568	26382	19820	20221	5347	37
29292	23652	24225	25678	26251	19689	20084	5594	50
29737	24097	24692	26174	25820	19258	19636	6538	60
30287	24647	25270	26786	25672	19110	19482	7304	70
30870	25230	25883	27436	25740	19178	19553	7883	90
34639	28999	29865	31656	18605	12043	12190	19466	920
34694	29054	29923	31718	18421	11859	12001	19717	980
34214	28574	29414	31179	18274	11712	11851	19328	1040
34404	28764	29616	31393	17661	11099	11224	20169	1170
34514	28874	29732	31516	16970	10408	10518	20998	1230
34447	28807	29661	31441	16233	9671	9765	21676	1350

TABLE 4.VII

(0.1040g; 1.46 mmol.) was attached to the line at position V_1 and the system pumped overnight. Before Cl_2 was admitted to the $FeCl_3$ (sample A), which had previously been in contact with $^{36}Cl_2$, the count from both GM tubes was monitored. After the addition of Cl_2 (0.0798g; 1.12 mmol. in the reaction vessel) the system was monitored for a further 5h. (Table 4.VIII). After this time, the chlorine was removed and the $FeCl_3$ analysed as outlined in section 2.3.2. The specific activity of the $FeCl_3$ was determined by precipitating the chloride ion as silver chloride and the $FeCl_3$ was found to be inactive.

4.2.4. $FeCl_3$ (sample B) AND $^{36}Cl_2$: EXCHANGE METHOD A.

The reaction between $FeCl_3$ (sample B) (0.7948g; 4.90 mmol.) and $^{36}Cl_2$ (0.1387g; 1.95mmol. in the reaction vessel) was performed by the method outlined in 4.2.2. and the system monitored over a period of 8.5h. (Table 4.IX). The specific activity of the $^{36}Cl_2$ was determined before and after the reaction.

4.2.5. $FeCl_3$ (sample B) and Cl_2: EXCHANGE METHOD A.

After the removal of $^{36}Cl_2$ from $FeCl_3$ (sample B), the reaction between the latter and Cl_2 (0.0915g; 1.29 mmol in the reaction vessel) was performed by the method outlined in 4.2.3. and the system monitored for 5h. (Table 4.X). The $FeCl_3$ was analysed and its specific activity determined. This sample was found to be inactive.

Results from Exchange Method A for $FeCl_3$ (Sample A) + Inactive Cl_2.

Counts(5min)$^{-1}$ in Solid & Gas Phases →	Counts(5min)$^{-1}$ -Background →	Counts(5min)$^{-1}$ Corrected for Dead Time →	Tubes Inter-calibrated	Counts(5min)$^{-1}$ in Gas Phase →	Counts(5min)$^{-1}$ -Background →	Counts(5min)$^{-1}$ Corrected for Dead Time	Surface Activity of $FeCl_3$ Counts(5min)$^{-1}$	Time Min
24535	18895	19259	20415	6832	270	270	20145	0
24387	18747	19105	20251	6719	157	157	20094	30
24497	18857	19219	20372	6801	239	239	20133	60
24606	18966	19333	20493	6754	192	192	20301	120
24558	18918	19283	20440	6843	281	281	20159	180
24642	19002	19370	20532	6901	339	339	20193	240
24663	19023	19392	20556	6907	345	345	20211	300

TABLE 4.VIII

RESULTS FROM EXCHANGE METHOD A FOR IRON(III) CHLORIDE (SAMPLE B)

Counts(100sec)$^{-1}$ in Solid & Gas Phases	Background	Corrected for Dead Time	Tubes inter-calibrated	Counts(100sec)$^{-1}$ in Gas Phase	Background	Corrected for Dead Time	Surface Activity of $FeCl_3$ Counts (100sec)$^{-1}$	Time Min.
14118	11404	11808	12753	10664	9053	9306	3447	0
13073	10359	10691	11546	10192	8581	8808	2738	5
15481	12767	13275	14337	9902	8291	8502	5835	10
14948	12234	12700	13716	9811	8200	8407	5309	15
15684	12970	13495	14575	9736	8125	8328	6247	20
16045	13331	13886	14997	9635	8024	8222	6775	30
16155	13441	14006	15126	9426	7815	8003	7123	45
16216	13502	14072	15198	8801	7190	7349	7849	60
16356	13642	14224	15362	8490	6879	7024	8338	79
17418	14704	15383	16614	7492	5881	5987	10627	150
17397	14683	15360	16589	6570	4959	5034	11555	180
17828	15114	15832	17099	6525	4914	4987	12112	210
18118	15404	16150	17442	6089	4478	4539	12903	240
17726	15012	15720	16978	5660	4049	4099	12879	275
18370	15656	16427	17741	5512	3901	3947	13794	320
18805	16091	16907	18260	5146	3535	3573	14687	390
19496	16782	17672	19086	4462	2851	2876	16210	510

TABLE 4.IX

Results from Exchange Method A for $FeCl_3$ (Sample B) + Inactive Cl_2.

Counts(100sec)$^{-1}$ in Solid & Gas Phases →	Counts(100sec)$^{-1}$ -Background →	Counts(100sec)$^{-1}$ Corrected for Dead Time →	Tubes Inter-calibrated	Counts(100sec)$^{-1}$ In Gas Phase →	Counts(100sec)$^{-1}$ -Background →	Counts(100sec)$^{-1}$ Corrected for Dead Time	Surface Activity of $FeCl_3$ counts(100sec)$^{-1}$	Time Min
16934	14220	14854	16043	1672	61	61	15982	0
17006	14292	14932	16127	1689	78	78	16049	30
16905	14191	14822	16008	1693	82	82	15926	60
16808	14094	14716	15894	1674	63	63	15831	130
16889	14175	14805	15990	1664	53	53	15937	180
16972	14258	14895	16087	1697	86	86	16001	240
16844	14130	14756	15937	1669	58	58	15879	300

TABLE 4.X

4.2.6. $FeCl_3$ (sample C) AND $^{36}Cl_2$: EXCHANGE METHOD A.

Using the method outlined in 4.2.2., the reaction between $FeCl_3$ (sample C) (0.5846g; 3.60 mmol.) and $^{36}Cl_2$ (0.1853g; 2.61 mmol in the reaction vessel) was monitored for 8h. (Table 4.XI). The specific activity of the $^{36}Cl_2$ was determined before and after the reaction.

4.2.7. $FeCl_3$ (sample C) AND Cl_2: EXCHANGE METHOD A.

After the removal of $^{36}Cl_2$ from $FeCl_3$ (sample C), the reaction between the latter and Cl_2 (0.1200g; 1.69 mmol in the reaction vessel) was performed by the method outlined in 4.2.3. and the system monitored over a period of 5h. (Table 4.XII). After this time the inactive Cl_2 was removed.

4.2.8. $FeCl_3$ (sample C) AND $CHCl_3$: EXCHANGE METHOD A.

After the removal of Cl_2 from $FeCl_3$ (sample C), the reaction between the latter and $CHCl_3$ vapour (0.4478g; 6.31 mmol in the reaction vessel) was performed by the method outlined in 4.2.3. and the system monitored for 6h. (Table 4.XIII). The $CHCl_3$ vapour was removed, the $FeCl_3$ analysed and its activity determined.

4.2.9. $FeCl_3$ (sample A) AND $^{36}Cl_2$: EXCHANGE METHOD B.

This reaction was performed using exchange method B (cf. 2.6.2.) and the apparatus shown in Figure 2.XVIII. This apparatus was pumped and flamed-out on a vacuum line before being transferred to an inert atmosphere dry box where a weighed amount of $FeCl_3$ (sample A) (1.5896g; 9.80 mmol) was placed in V_1. The vessel was transferred

RESULTS FROM EXCHANGE METHOD A FOR IRON(III) CHLORIDE (SAMPLE C)

Counts(100sec)$^{-1}$ in Solid & Gas Phases	± Background	Corrected for Dead Time	Counts(100sec)$^{-1}$ in Gas Phase	± Background	Corrected for Dead Time	Tubes Inter-calibrated	Surface Activity of $FeCl_3$ Counts (100sec)$^{-1}$	Time Min.
27234	26547	28844	18878	18360	19430	21373	7471	0
24776	24089	25965	18338	17820	18826	20709	5256	10
26249	25562	27685	18441	17923	18942	20836	6849	12
25445	24758	26745	17379	16861	17759	19535	7210	15
23870	23183	24916	14591	14073	14693	16162	8754	80
23411	22724	24386	13259	12741	13247	14572	9814	115
24011	23324	25079	12837	12319	12792	14071	11008	150
23961	23274	25021	11426	10908	11277	12405	12616	225
26507	25820	27988	11113	10595	10943	12037	15951	278
26535	25848	27595	10470	9952	10258	11284	16311	335
29374	28687	31388	8877	8359	8574	9431	21957	485

TABLE 4.XI

Results from Exchange Method A for $FeCl_3$ (Sample C) + Inactive Cl_2.

Counts(100sec)$^{-1}$ in Solid & Gas Phases →	Counts(100sec)$^{-1}$ -Background →	Counts(100sec)$^{-1}$ Corrected for Dead Time	Counts(100sec)$^{-1}$ in Gas Phase →	Counts(100sec)$^{-1}$ -Background →	Counts(100sec)$^{-1}$ Corrected for Dead Time →	Tubes Inter-calibrated	Surface Activity of $FeCl_3$ Counts(100sec)$^{-1}$	Time Min
19639	18952	20095	569	51	51	56	20039	0
19533	18846	19975	573	55	55	61	19914	30
19571	18884	20018	554	36	36	40	19978	60
19622	18935	20076	589	71	71	78	19998	120
19719	19032	20184	591	73	73	80	20104	180
19485	18798	19921	557	39	39	43	19878	240
19654	18967	20111	561	43	43	47	20064	300

TABLE 4.XII

Results from Exchange Method A for $FeCl_3$ (Sample C) + Inactive $CHCl_3$.

Counts(100sec)$^{-1}$ in Solid & Gas Phases →	Counts(100sec)$^{-1}$ -Background →	Counts(100sec)$^{-1}$ Corrected for Dead Time	Counts(100sec)$^{-1}$ in Gas Phase →	Counts(100sec)$^{-1}$ -Background →	Counts(100sec)$^{-1}$ Corrected for Dead Time →	Tubes Inter-calibrated	Surface Activity of $FeCl_3$ Counts(100sec)$^{-1}$	Time Min
19679	18992	20139	598	80	80	88	20051	0
19601	18914	20052	613	95	95	105	19947	30
19703	19016	20166	573	55	55	61	20105	60
19629	18942	20088	581	63	63	69	20014	120
19425	18738	19854	532	14	14	15	19839	180
19653	18966	20110	569	51	51	56	20054	240
19678	18991	20138	554	36	36	40	20098	300

TABLE 4.XIII

to a vacuum line and evacuated before the addition of $^{36}Cl_2$ (0.4544g; 6.40 mmol). The initial specific activity of the $^{36}Cl_2$ was determined, by converting a sample to Cl^- and precipitating it as $Ag^{36}Cl$, before it was added to the $FeCl_3$. The exchange vessel was stored in a thermostat bath at 298K. The specific activity of $^{36}Cl_2$ was monitored periodically by attaching the exchange vessel to the vacuum line and allowing the gas into V_2 at room temperature. The ratio $V_1:V_2$ was known accurately, hence the amount of $^{36}Cl_2$ in V_2 was calculated. The $^{36}Cl_2$ contained in V_2 was distilled into a NaOH solution at 77K , precipitated as $Ag^{36}Cl$ and its specific activity determined. This process was repeated a number of times. (Table 4.XIV). After all the $^{36}Cl_2$ was removed, the $FeCl_3$ was hydrolysed, the iron precipitated as iron oxide and the chloride ion as silver chloride. The ^{36}Cl specific activity in $FeCl_3$ was determined as AgCl.

4.2.10. $FeCl_3$ (sample B) AND $^{36}Cl_2$: EXCHANGE METHOD B.

The reaction between $FeCl_3$ (sample B) (0.5790g; 3.57 mmol.) and $^{36}Cl_2$ (0.1565g; 2.20 mmol) was performed as outlined in 4.2.9. The $^{36}Cl_2$ was removed at intervals, precipitated as $Ag^{36}Cl$ and its specific activity determined. (Table 4.XV). At the end of the reaction, the $FeCl_3$ was analysed by precipitation of the iron as Fe_2O_3 and of the chloride ion as AgCl. The specific activity of $FeCl_3$ was determined as AgCl.

RESULTS FROM EXCHANGE METHOD B FOR IRON(III) CHLORIDE (SAMPLE A)

Sample	(1) Amount AgCl Counted mg.	(1) Corrected * Count Counts (300sec)$^{-1}$	(1) Counts (300(sec)$^{-1}$ mg^{-1}	(1) Corrected for Self Absorption	(2) Amount of AgCl Counted mg.	(2) Corrected * Count Counts(300sec)$^{-1}$	(2) Counts(300sec)$^{-1}$ mg^{-1}	(2) Corrected for Self Absorption	Average Counts (300sec)$^{-1}$ mg^{-1}	Time h.
Initial	26.4	10439	395	610	22.0	9900	450	597	604	0
1st.	18.9	5955	315	371	17.3	6228	360	403	387	5.5
2nd.	23.3	7153	307	429	23.7	7323	309	435	432	30.25
Final	24.2	7514	310	448	21.6	7106	329	433	440	119

* Corrected count :- Corrected for Background + Dead Time.

Initial Stoichiometry :- 9.8 mmol of $FeCl_3$: 6.4 mmol of $^{36}Cl_2$

Final Stoichiometry :- 9.8 mmol of $FeCl_3$: 4.8 mmol of $^{36}Cl_2$

TABLE 4.XIV

RESULTS FROM EXCHANGE METHOD B FOR IRON(III) CHLORIDE (SAMPLE B)

Sample	(1) Amount AgCl Counted mg	(1) *Corrected Count Counts (300sec)$^{-1}$	(1) Counts(300sec)$^{-1}$ mg^{-1}	(1) Corrected for Self Absorption	(2) Amount AgCl Counted mg	(2) *Corrected Count Counts(300sec)$^{-1}$	(2) Counts (300sec)$^{-1}$ mg^{-1}	(2) Corrected for Self Absorption	Average Counts (300sec)$^{-1}$ mg^{-1}	Time h.
Initial	23.1	36502	1580	2176	23.9	35905	1502	2134	2155	0
1st.	21.4	29864	1396	1811	19.4	28758	1482	1792	1802	20.33
2nd.	22.5	31710	1409	1911	19.8	26972	1362	1670	1790	45.25
3rd.	22.4	32616	1456	1968	21.9	28098	1283	1694	1831	165.83
4th	24.2	34640	1431	2066	27.7	38010	1372	2193	2130	219.25
Final	26.7	34123	1278	1982	23.7	33250	1403	1977	1980	455.33

* Corrected Count :- Corrected for Background + Dead Time

Initial Stoichiometry :- 3.57 mmol. $FeCl_3$: 2.2 mmol. $^{36}Cl_2$

Final Stoichiometry :- 3.57 mmol. $FeCl_3$: 1.08 mmol. $^{36}Cl_2$

TABLE 4.XV

4.2.11. $FeCl_3$ (sample C) AND $^{36}Cl_2$: EXCHANGE METHOD B.

The reaction between $FeCl_3$ (sample C) (0.4641g; 2.86 mmol) and $^{36}Cl_2$ (0.2712g; 3.82 mmol) was performed as outlined in 4.2.9. The $^{36}Cl_2$ was removed at intervals, precipitated as $Ag^{36}Cl$ and its specific activity determined. (Table 4.XVI). After the $^{36}Cl_2$ was removed, the $FeCl_3$ was analysed by precipitating the iron as Fe_2O_3 and the chloride ion as AgCl and its specific activity determined.

4.2.12. $FeCl_3|CH_3CN|^{36}Cl_2$: RUN I.

This reaction was performed using exchange method B (cf. 2.6.2.) and the apparatus shown in Figure 2.XVIII. This apparatus was pumped and flamed out on a vacuum line before being transferred to an inert atmosphere dry box. In the dry box, a solution of $FeCl_3$ in CH_3CN was prepared by weighing $FeCl_3$ (0.1622g; 1.00 mmol) into a 50ml standard flask and dissolving it in acetonitrile. The concentration of the solution was 2.0×10^{-2} mol L^{-1}. This solution was transferred to V_1 of the exchange vessel. The vessel was removed from the dry box and the solution degassed twice before a weighed amount of $^{36}Cl_2$ (0.5886g; 8.29 mmol) was admitted. The initial specific activity of the $^{36}Cl_2$ was determined before the addition. The exchange vessel was thermostated at 298K. After 6h. the exchange vessel was attached to the vacuum line and the $FeCl_3|CH_3CN$ solution held at 209.5K by a chloroform slush bath. The $^{36}Cl_2$ was removed by allowing the gas into V_2, converted to $^{36}Cl^-$(aq), precipitated as $Ag^{36}Cl$

RESULTS FROM EXCHANGE METHOD B FOR IRON(III) CHLORIDE (SAMPLE C)

Sample	(1) Amount AgCl Counted mg	(1) * Corrected Count Counts (300sec)$^{-1}$	(1) Counts(300sec)$^{-1}$ mg^{-1}	(1) Corrected for Self Absorption	(2) Amount AgCl counted mg	(2) * Corrected Count Counts (300sec)$^{-1}$	(2) Counts(300sec)$^{-1}$ mg^{-1}	(2) Corrected for Self Absorption	Average Counts (300sec)$^{-1}$ mg^{-1}	Time h.
Initial	24.2	24952	1031	1476	25.4	25349	998	1488	1482	0
1st.	21.4	21687	1013	1314	20.5	21439	1046	1304	1309	6
2nd.	24.4	23518	964	1392	29.2	26922	922	1542	1467	25.75
3rd	23.8	25164	1057	1502	22.2	22602	1018	1360	1431	29.75
4th	23.1	21389	926	1275	19.5	20238	1038	1255	1265	152.66
Final	19.2	19139	997	1179	16.0	16994	1062	1118	1148	431.33

* Corrected Count :- Corrected for Background + Dead Time

Initial Stoichiometry :- 2.86 mmol. $FeCl_3$: 3.82 mmol. $^{36}Cl_2$

Final Stoichiometry :- 2.86 mmol. $FeCl_3$: 2.47 mmol. $^{36}Cl_2$

TABLE 4.XVI

and its specific activity determined. The procedure was repeated at intervals until the amount of $^{36}Cl_2$ collected became too small to count accurately. (Table 4.XVII). After 30h, the solvent was removed by vacuum distillation at 77K. The remaining solid was analysed by hydrolysing the sample, the iron was precipitated as Fe_2O_3 and the chloride ion as AgCl. The specific activity of the $FeCl_3$ was determined as AgCl. (Table 4.XVII).

4.2.13. $FeCl_3|CH_3CN|^{36}Cl_2$: RUN II.

A solution (50 ml) of $FeCl_3$ in acetonitrile was prepared as outlined in 4.2.12. The concentration of the solution was 2.0×10^{-2} mol l^{-1}. The initial specific activity of $^{36}Cl_2$ was determined before a weighed amount (0.4217g; 5.94 mmol) was added to the solution. Samples of $^{36}Cl_2$ were removed at intervals and its specific activity determined as $Ag^{36}Cl$, until the amount of $^{36}Cl_2$ collected became too small to count accurately. (Table 4.XVIII.) After 42h. the solvent was removed by vacuum distillation at 77K. The remaining solid was analysed by hydrolysing the sample, the iron precipitated as Fe_2O_3 and the chloride ion as AgCl. The specific activity of the $FeCl_3$ was determined as AgCl.

4.2.14. ANALYSIS OF IRON'S OXIDATION STATE IN $FeCl_3|CH_3CN$ AND $FeCl_3|CH_3CN|Cl_2$.

In the inert atmosphere box, a solution of

RESULTS FROM EXCHANGE REACTION:- RUN I

Sample	Time	Colour	%Cl Recovered	Amount AgCl Counted(1) (mg)	Corrected* Count Counts(300sec)$^{-1}$ (1)	Counts(300sec)$^{-1}$ mg^{-1} (1)	Corrected for Self Absorption (1)	Amount AgCl Counted (2)	Corrected* Count Counts(300sec)$^{-1}$ (2)	Counts(300sec)$^{-1}$ mg^{-1} (2)	Corrected for Self Absorption (2)	Average Count Counts(300sec)$^{-1}$ mg^{-1}
Initial	0	Red	94.6	17.5	12974	741	829	18.3	14139	773	887	858
1st	3.25h	Red	52.0	11.7	7445	636	558	13.4	8174	610	564	561
2nd.	20.5h	Orange	31.8	12.4	8053	650	587	-	-	-	-	587
Remaining Solid	After Solvent Removal	-	121.1	17.3	10387	600	671	17.6	10724	609	686	678

* Corrected Count :- Corrected for Background + Dead Time

where %Cl Recovered = $\frac{\text{AgCl Obtained}}{\text{AgCl Required}} \times 100$

TABLE 4.XVII

RESULTS FROM EXCHANGE REACTION:- RUN II

Sample	Time	Colour	% Cl Recovered ±	Amount AgCl Counted (mg) (1)	Corrected Count Counts(300sec)$^{-1}$ (1) ±	Counts(300sec)$^{-1}$ mg^{-1} (1) ±	Corrected for Self Absorption (1)	Amount AgCl Counted (mg) (2) ±	Corrected Count Counts(300sec)$^{-1}$ (2) ±	Counts(300sec)$^{-1}$ mg^{-1} (2) ±	Corrected for Self Absorption (2)	Average Count $^{-1}$ $^{-1}$ Counts(300sec) mg
Initial	0	Red	98.3	15.5	10961	707	727	13.6	9772	718	684	706
1st	2h.	Red	80.1	10.0	5806	581	464	15.4	7350	477	491	478
2nd.	6.16h	Orange	43.7	17.4	6066	349	390	15.2	5590	368	374	382
Remaining Solid	After Solvent Removal	-	130.4	18.4	10005	544	632	19.1	10490	549	651	642

where %Cl recovered = $\frac{\text{AgCl Obtained}}{\text{AgCl Recovered}}$ x 100

TABLE 4.XVIII

$FeCl_3$ in CH_3CN was prepared by weighing $FeCl_3$ (0.1622g; 1.00 mmol) into a 50ml standard flask and adding acetonitrile. The concentration of this solution was 2.0×10^{-2} mol l^{-1}. A series of 5ml aliquots was removed and diluted to 50ml with acetonitrile. The concentration of Fe in each of these solutions was 11.2 mg l^{-1}. The solutions were placed in rotaflo vessels, which had been pumped and flamed out previously; they were then transferred to a vacuum system where they were degassed twice. Weighed amounts of Cl_2 (Table 4.XXXVI) were distilled into half of these solutions at 77K. The two systems, that is $FeCl_3|CH_3CN$ and $FeCl_3|CH_3CN|Cl_2$, were examined for the presence of Fe^{II} and total Fe, at various stages of the reaction by the method outlined in section 2.3.3.

4.2.15. ELECTRONIC SPECTRA OF $FeCl_3|CH_3CN$ AND $FeCl_3|CH_3CN|Cl_2$.

Two U.V. cells (Fig. 2.III) were pumped and flamed-out before being transferred to an inert atmosphere box. Two solutions with a concentration of 1.0×10^{-1} mol l^{-1} were prepared as 5 ml solutions of $FeCl_3$ in CH_3CN. $FeCl_3$ (0.0811g; 0.50 mmol) was weighed into a 5ml standard flask and dissolved in CH_3CN. The solutions were placed in the UV cells and transferred to a vacuum system where they were degassed twice. A weighed amount of Cl_2 (0.1543g; 2.17 mmol) was added to one of the UV cells by holding the solution of $FeCl_3$ in CH_3CN at 77K and distilling the $^{36}Cl_2$ into the cell. Both solutions were monitored over a period of time.

4.2.16. G.L.C. ANALYSIS OF $CH_3CN|Cl_2$, $FeCl_3|CH_3CN$ AND $FeCl_3|CH_3CN|Cl_2$.

Three rotaflo vessels were pumped and flamed out on a vacuum line before being transferred to an inert atmosphere box. Two solutions (10 ml) of $FeCl_3$ in CH_3CN were prepared by weighing $FeCl_3$ (0.0324g; 0.20 mmol) in a 10 ml standard flask and adding analar CH_3CN. The solution's concentration was 2.0×10^{-2} mol l^{-1}. A further 10 ml of CH_3CN was measured into an empty 10 ml standard flask. These three samples were placed in the rotaflo vessels and transferred to a vacuum system where they were degassed twice. A weighed amount of Cl_2 (0.1278 g; 1.80 mmol.) was distilled into the vessel containing acetonitrile and another (0.1775g; 2.50 mmol) into one of the $FeCl_3|CH_3CN$ solutions. These three flasks were stored in a thermostat bath at 298K for 20h. before the chlorine was removed by holding the solutions at 209.5K and distilling the Cl_2 at 77K. The solvent from each mixture was removed by vacuum distillation at 77K and examined by GLC for the presence of monochloroacetonitrile and trichloroacetonitrile. The GLC work was performed under the conditions shown in Table 4.XIX. A calibration curve relating the measured peak height to the amount of CH_2ClCN present in CH_3CN was obtained by making up solutions with known concentrations of CH_2ClCN in CH_3CN and measuring the size of peak obtained. (Figure 4.I). The peak heights observed for CH_2ClCN in these three systems are shown in Table 4.XX. No CCl_3CN was detected in any of these solutions.

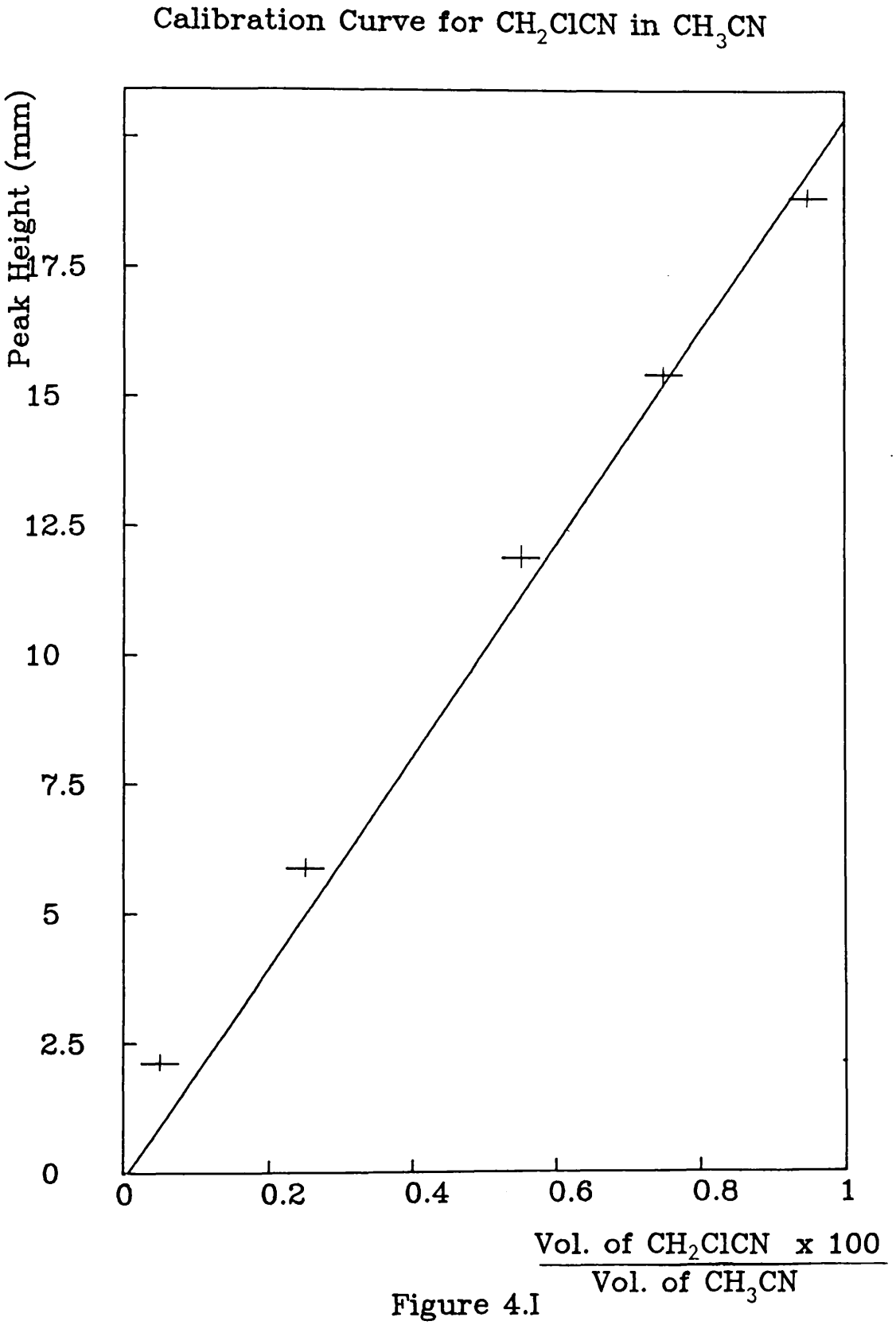

Calibration Curve for CH_2ClCN in CH_3CN
Peak Height (mm)
17.5
15
12.5
10
7.5
5
2.5
0
0
0.2
0.4
0.6
0.8
1
Vol. of CH_2ClCN x 100
Vol. of CH_3CN

Figure 4.I

PEAK HEIGHTS OF CH_2ClCN

System	CH_2ClCN Peak Height mm	$\frac{\text{Vol. of } CH_2ClCN}{\text{Vol of } CH_3CN} \times 100$
$CH_3CN \mid Cl_2$	3.5	0.016
$FeCl_3 \mid CH_3CN$	-	-
$FeCl_3 \mid CH_3CN \mid Cl_2$	55.5	0.290

TABLE 4.XX

GLC ANALYSIS CONDITIONS

Performed on	Pye Unicam GCD Chromatograph
Column	9' by ¼" Glass, 15% carbowax on universal support
Temperature	131°C
Carrier Gas	Nitrogen
Carrier Flow	40 ml min^{-1}
Injection Size	1 µl

TABLE 4.XIX

4.2.17. G.L.C. ANALYSIS OF $FeCl_3|CH_3CN|Cl_2$ USING VARYING AMOUNTS OF Cl_2.

Five rotaflo vessels were pumped and flamed out on a vacuum system before being transferred to a dry box. Fifty ml of a solution of $FeCl_3$ in CH_3CN was prepared by weighing $FeCl_3$ (0.1622g; 1.00 mmol.) in a 50 ml standard flask and adding analar acetonitrile. A 5ml aliquot of this solution was pipetted into each of the rotaflo vessels. Each solution had a concentration of 2.0×10^{-2} mol^{-1}. The vessels were transferred to a vacuum system where they were degassed twice before adding weighed amounts of Cl_2. The vessels were stored in a thermostat bath at 298K for 7 days after which the Cl_2 was removed. The solvent from each was distilled into a trap at 77K. and examined by GLC for the presence of CH_2Cl CN and CCl_3CN. The GLC work was performed under the conditions shown in Table 4.XXI and calibration curves were constructed for both CH_2ClCN and CCl_3CN in CH_3CN. (Figures 4II + 4III). In this calibration, toluene was used as the internal standard as outlined in Section 2.7. The peak height ratios observed for both CH_2ClCN and CCl_3CN are shown in Table 4XXII.

GLC ANALYSIS CONDITIONS

Performed on	Carlo Erba Capillary GC Unit Fractovap 2351 AC
Column	50 m carbowax 20M on glass
Temperature	111°C
Carrier Gas	Helium
Carrier Flow	2 ml min^{-1}
Split Mode	50/1 (1 through column)
Injection Size	10 µl
Internal Standard	100 µl Toluene (AR) TO 50 ml SAMPLE.

TABLE 4.XXI

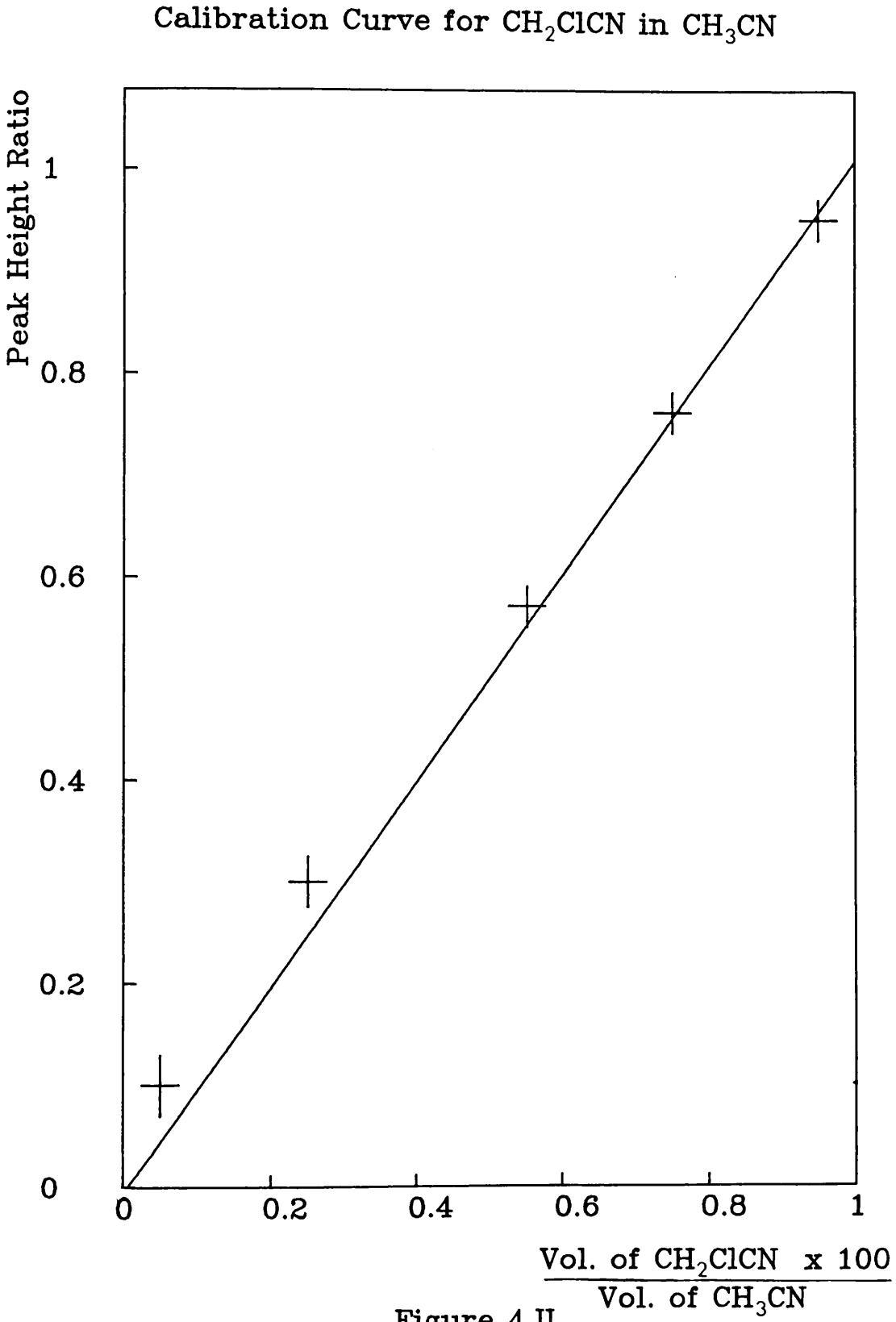

Calibration Curve for CH_2ClCN in CH_3CN
Peak Height Ratio
1
0.8
0.6
0.4
0.2
0
0
0.2
0.4
0.6
0.8
1
Vol. of CH_2ClCN x 100
Vol. of CH_3CN

Figure 4.II

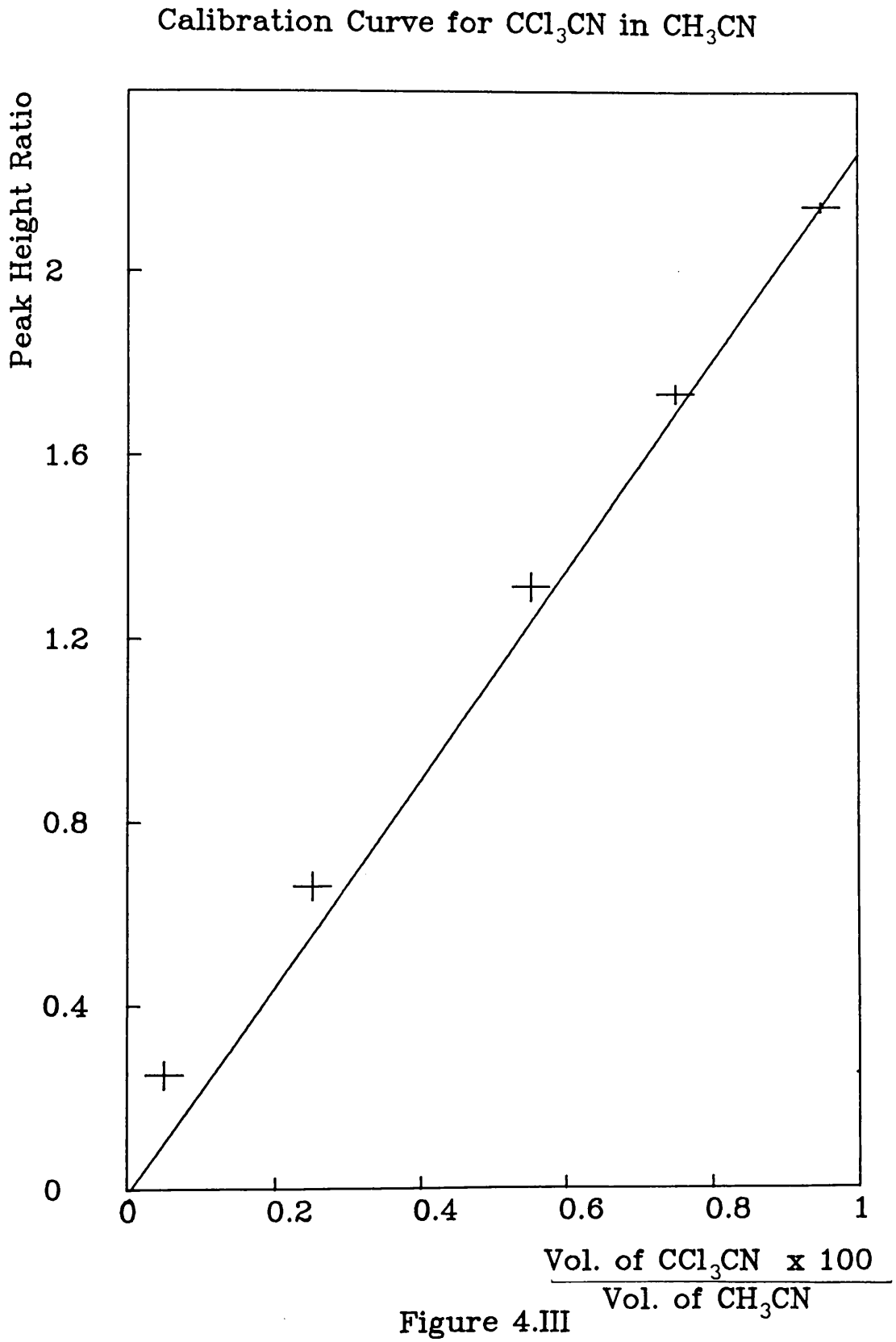

Calibration Curve for CCl_3CN in CH_3CN
Peak Height Ratio
0
0.4
0.8
1.2
1.6
2
0
0.2
0.4
0.6
0.8
1
Vol. of CCl_3CN x 100
Vol. of CH_3CN

Figure 4.III

GLC RESULTS FROM THE $FeCl_3|CH_3CN|Cl_2$ SYSTEM.

Amount Cl_2 Added mmol	Peak Height Ratio CH_2ClCN:IS	$\frac{vol.CH_2ClCN}{vol.CH_3CN}$ x100	Peak Height Ratio CCl_3CN: IS:	$\frac{vol.CCl_3CN}{vol.CH_3CN}$ x100
0.915	0.375	0.392	0.338	0.160
2.14	0.505	0.332	0.237	0.112
2.99	0.473	0.494	0.710	0.332
4.91	0.398	0.418	0.866	0.405
6.40	0.055	0.046	1.95	0.900

TABLE 4.XXII

4.2.18. G.L.C. ANALYSIS OF $[Fe(CH_3CN)_6][PF_6]_2|CH_3CN|Cl_2$ USING VARYING AMOUNTS OF Cl_2.

In a dry box, 50 ml of a solution of $[Fe(CH_3CN)_6][PF_6]_2$ in CH_3CN was prepared by weighing $[Fe(CH_3CN)_6][PF_6]_2$ (0.5920g; 1.00 mmol) in a 50 ml standard flask and adding analar acetonitrile. The concentration of the solution was 2.0×10^{-2} mol l^{-1}. The analysis was performed by the method outlined in 4.2.17 using identical GLC conditions (Table 4.XXI) and calibration curves. (Figures 4.II + 4.III). The peak height

ratios observed for both CH_2ClCN and CCl_3CN are shown in Table 4.XXIII.

G.L.C. RESULTS FROM THE $[Fe(CH_3CN)_6][PF_6]_2|CH_3CN|Cl_2$ SYSTEM.

Amount Cl_2 Added mmol.	Peak Height Ratio CH_2ClCN: IS	$\frac{vol.CH_2ClCN}{vol.CH_3CN}$ x100	Peak Height Ratio CCl_3CN: IS	$\frac{vol.CCl_3CN}{vol.CH_3CN}$ x100
1.15	0.685	0.725	-	-
2.53	0.833	0.863	-	-
2.86	0.853	0.906	-	-
4.17	0.449	0.472	0.163	0.080
4.54	0.410	0.430	0.175	0.086
14.30	0.091	0.090	0.717	0.335

TABLE 4.XXIII

4.3. RESULTS FROM THE HETEROGENEOUS REACTIONS

Hetereogeneous reactions between $FeCl_3$ and $^{36}Cl_2$ have been monitored by two different techniques.

4.3.1. EXCHANGE METHOD A

In this method the interaction between $^{36}Cl_2$ and $FeCl_3$ is monitored by two G.M. tubes contained in an evacuable counting vessel which has been described earlier (cf. 2.6.1., Fig. 2.XV). 36-Chlorine exchange between $^{36}Cl_2$ and $FeCl_3$ or adsorption of $^{36}Cl_2$ on the solid results in an increased count from the tube monitoring the solid plus gas and a decreased count from that monitoring the gas phase alone.

When a known pressure (34mm) of $^{36}Cl_2$ (0.0654g; 0.92 mmol) is admitted to the reaction vessel in the absence of $FeCl_3$, the count rates from both GM tubes decrease. (Figure 4.IV). After the removal of $^{36}Cl_2$, the surface activity of the glass is greater than the initial background which indicates that $^{36}Cl_2$ is adsorbed by the glass reaction vessel. When a second sample of $^{36}Cl_2$ (0.0596g; 0.84 mmol) is admitted to the reaction vessel, the decrease in the count rate is not so great as in the previous reaction (Figure 4.IV) but the surface activity of the glass again increases. After the third exposure of the reaction vessel to $^{36}Cl_2$ (0.0569g; 0.80 mmol) the decrease in the count rate is much less (Figure 4.IV) which indicates that less $^{36}Cl_2$ is adsorbed by the reaction vessel. The surface activity of the vessel has again increased though this value decreases slightly after overnight pumping.

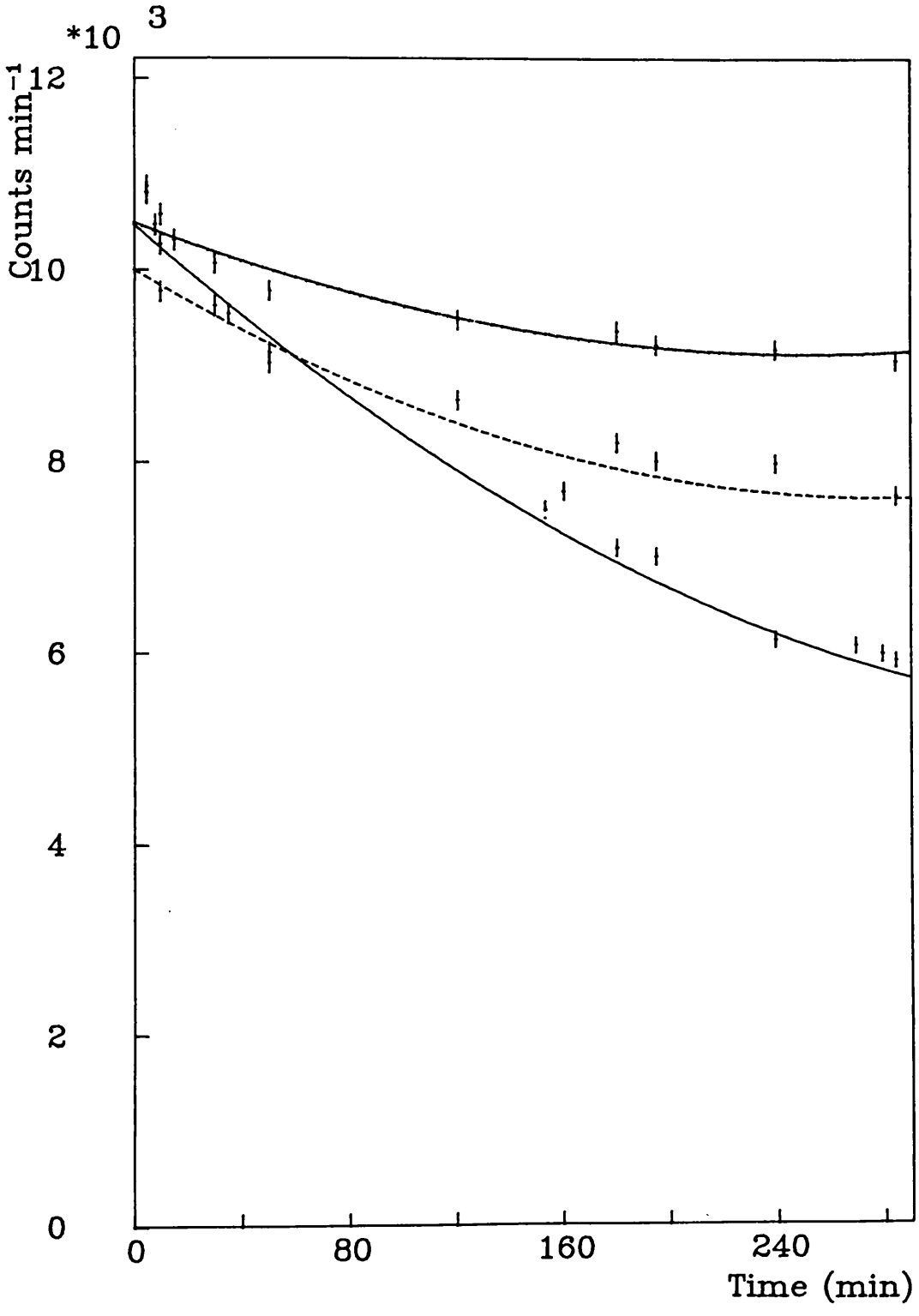

Adsorption of $^{36}Cl_2$ by the Reaction Vessel
*10 3
Counts min^{-1}
12
10
8
6
4
2
0
0
80
160
240
Time (min)

Figure 4.IV

After exposure to $^{36}Cl_2$, the GM tubes used in the reaction vessel also exhibit surface activity.

These results show that $^{36}Cl_2$ is adsorbed on to the reaction vessel and, therefore, pretreatment of the vessel with $^{36}Cl_2$ is essential before the reaction between $FeCl_3$ and $^{36}Cl_2$ is performed.

When a known pressure (37 mm) of $^{36}Cl_2$ (0.0701g; 0.99 mmol) is admitted to $FeCl_3$ (Sample A, prepared from iron wire + Cl_2) (0.9805g; 6.04 mmol) the count rate from the gas plus solid increases with time and that from the gas alone decreases (Figure 4.V). The difference in count rates gives the surface ^{36}Cl activity of $FeCl_3$, and the variation of this with time is shown in Figure 4.VI. The surface activity is unaffected by the removal of $^{36}Cl_2$ from the gas phase and also by the introduction of a fresh sample of inactive Cl_2. Analysis of the $FeCl_3$ after Cl_2 has been removed indicates that the ratio Fe:Cl is 1:3.0 (Table 4.XXIV) and that $FeCl_3$ is inactive (Table 4.XXV). 36-Chlorine exchange, therefore, has not occurred under the conditions used but $^{36}Cl_2$ is adsorbed by the $FeCl_3$. The amount of $^{36}Cl_2$ adsorbed can be estimated as shown in the following calculation.

After 22h, the surface activity of $FeCl_3$ (sample A) = 72 counts sec^{-1}. From the graph showing the pressure of $^{36}Cl_2$ vs counts (Figure 4.VII) it can be seen that 72 counts $sec^{-1} \equiv$ 30.5 mm. Assuming that the counting efficiency in gas $\equiv$ counting efficiency in solid, then the number of mmol of $^{36}Cl_2$ present = $\frac{PV}{RT}$

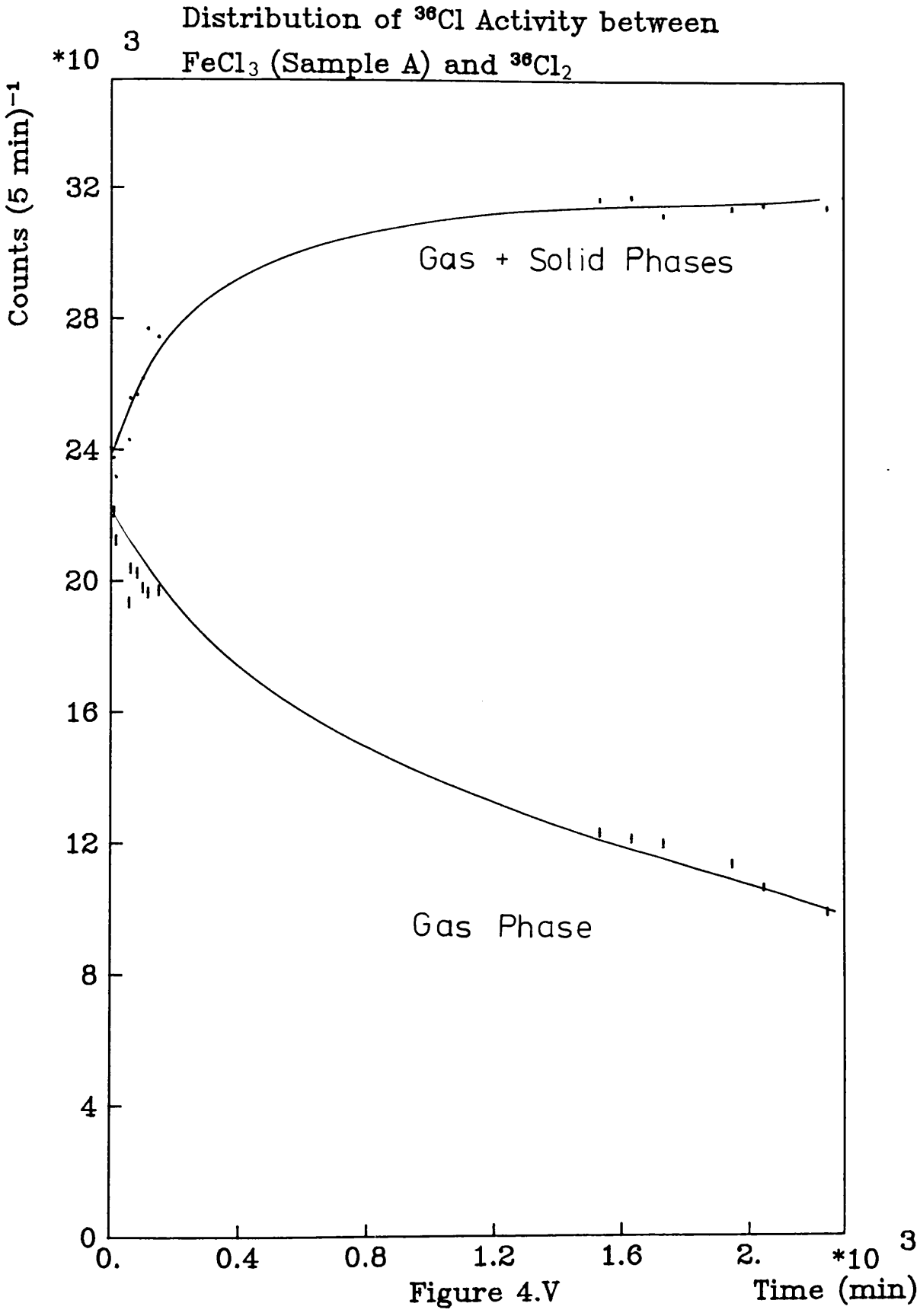

Distribution of ^{36}Cl Activity between
$FeCl_3$ (Sample A) and $^{36}Cl_2$
*10 3
Counts (5 min)$^{-1}$
32
28
24
20
16
12
8
4
0
Gas + Solid Phases
Gas Phase
0.
0.4
0.8
1.2
1.6
2.
*10 3
Time (min)

Figure 4.V

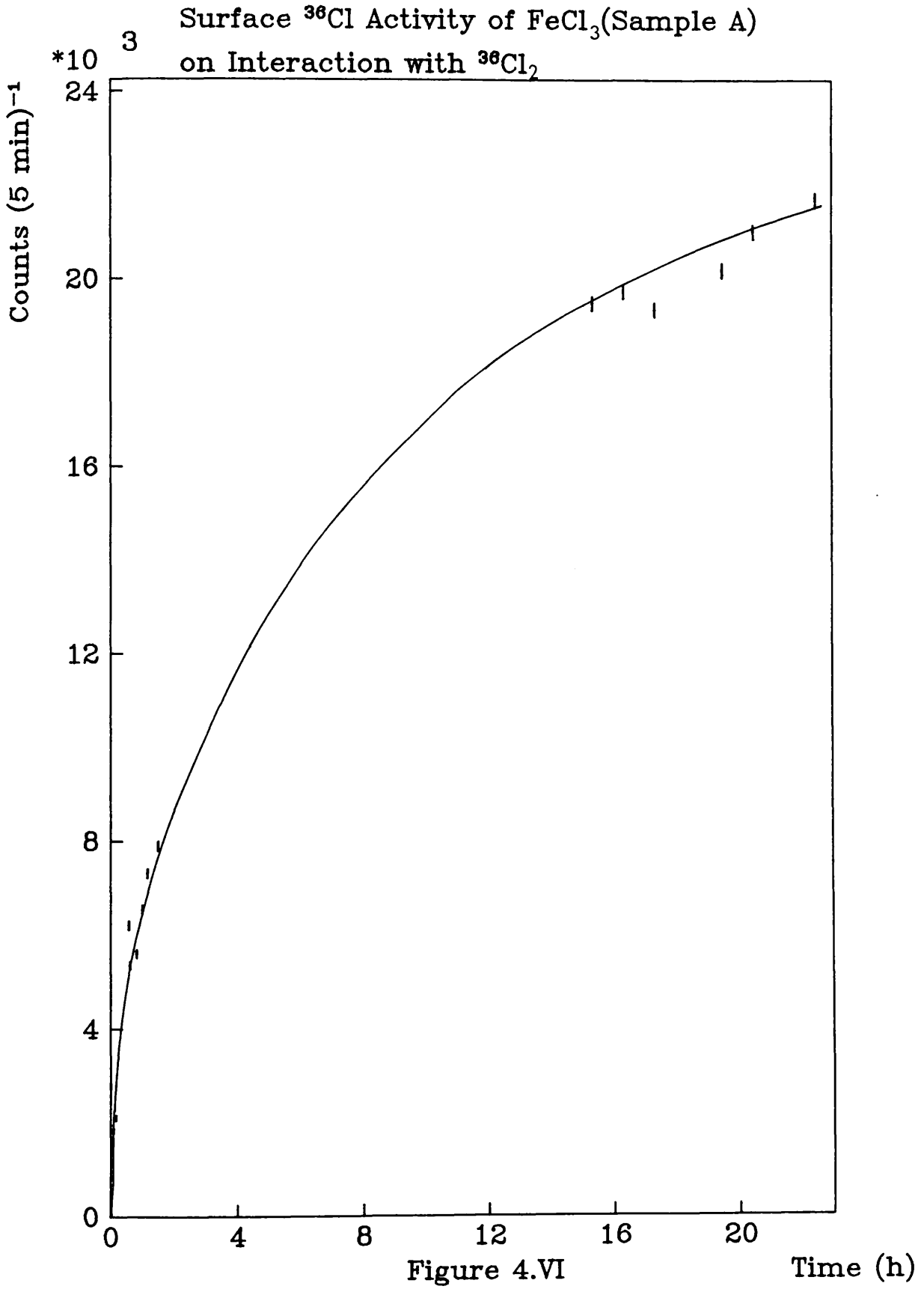

Surface ^{36}Cl Activity of $FeCl_3$(Sample A)
on Interaction with $^{36}Cl_2$
*10 3
Counts (5 min)$^{-1}$
24
20
16
12
8
4
0
0
4
8
12
16
20
Time (h)

Figure 4.VI

ANALYSIS OF $FeCl_3$ SAMPLES FROM EXCHANGE METHOD A

	CHLORINE		IRON	
	% Obtained	% Required for $FeCl_3$	% Obtained	% Required for $FeCl_3$
$FeCl_3$ (Sample A)	63.2	65.6	32.1	34.4
$FeCl_3$ (Sample B)	63.1	65.6	33.0	34.4
$FeCl_3$ (Sample C)	63.5	65.6	33.5	34.4

TABLE 4.XXIV

SPECIFIC ACTIVITIES OF THE REACTANTS FROM EXCHANGE METHOD A

	Specific Activity from Initial Chlorine Counted as $Ag^{36}Cl$ Counts $min^{-1}mg^{-1}$.	Specific Activity from Final Chlorine Counted as $Ag^{36}Cl$ Counts $min^{-1}mg^{-1}$.	Specific Activity from $FeCl_3$. Counted as $Ag^{36}Cl$. Counts $min^{-1}mg^{-1}$.
$FeCl_3$ (Sample A)	233 ± 13	215 ± 12	0.9 ± 0.6
$FeCl_3$ (Sample B)	347 ± 14	311 ± 14	1.1 ± 0.7
$FeCl_3$ (Sample C)	129 ± 11	115 ± 11	1.2 ± 0.8

TABLE 4.XXV

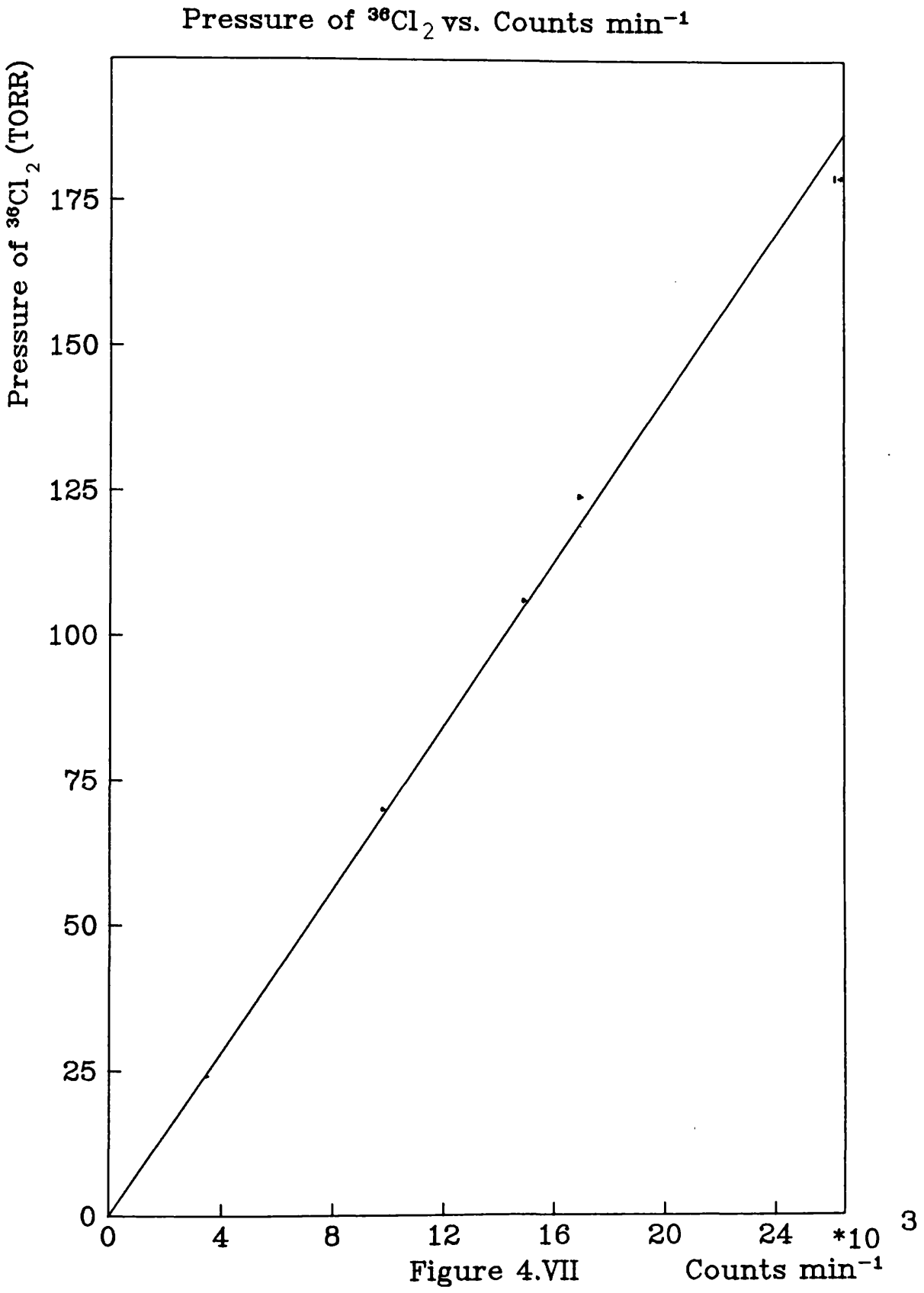

Pressure of $^{36}Cl_2$ vs. Counts min^{-1}
Pressure of $^{36}Cl_2$ (TORR)
0
25
50
75
100
125
150
175
0
4
8
12
16
20
24
*10 3
Counts min^{-1}

Figure 4.VII

where P = pressure of $^{36}Cl_2$

V = volume of reaction vessel (ml).

R = gas constant (82.053 ml atm K^{-1} mol^{-1})

T = temperature (K)

The number of mmol of $^{36}Cl_2$ present = $\frac{0.040 \times 498.7}{82.053 \times 297}$

$$= \underline{0.82 \text{ mmol}}$$

The number of $^{36}Cl_2$ molecules = $0.82 \times 10^{-3} \times 6.022 \times 10^{23}$

$$= \underline{4.94 \times 10^{20}}$$

The weight of $FeCl_3$ (sample A) = 0.9805 g

Surface area of $FeCl_3$ (sample A) = $0.15 m^2 g^{-1}$

Therefore, the surface area of this sample = 0.9805×0.15

$$= 0.147 m^2$$

$$= \underline{0.147 \times 10^{20} \text{Å}^2}$$

From single crystal and powder pattern X-ray studies,[62] it can be deduced that there are 3 Fe atoms per unit cell, that is, 3 Fe atoms in 93.53Å^2. Assuming for a monolayer coverage, that one $^{36}Cl_2$ is adsorbed by one Fe atom, then if

93.53Å^2 corresponds to 3 Fe atoms

$0.147 \times 10^{20} \text{Å}^2$ corresponds to 4.72×10^{17} Fe atoms.

Therefore 4.72×10^{17} molecules of $^{36}Cl_2$ are required for monolayer coverage. The number of $^{36}Cl_2$ molecules adsorbed by the surface was 4.94×10^{20}, which is more than is required for monolayer coverage.

When $^{36}Cl_2$ (0.1387g; 1.95 mmol) is admitted to $FeCl_3$ (sample B, prepared by $SOCl_2$ dehydration of $FeCl_3.6H_2O$)

(0.7948g; 4.90 mmol) the count rate from the gas plus solid increases with time and that from the gas alone decreases. The variation of the surface ^{36}Cl activity of $FeCl_3$ with time is shown in Figure 4.VIII. The surface activity is unaffected by the removal of $^{36}Cl_2$ from the gas phase and also by the introduction of a fresh sample of inactive Cl_2. Analysis of the $FeCl_3$ after Cl_2 has been removed indicates that the ratio Fe:Cl is 1:3.0 (Table 4.XXIV) and that $FeCl_3$ is inactive (Table 4.XXV). 36-Chlorine exchange, therefore, has not occurred under the conditions used but $^{36}Cl_2$ is adsorbed by the $FeCl_3$. The amount of $^{36}Cl_2$ adsorbed can be estimated as shown in the following calculation.

After 8.5h, the surface activity of $FeCl_3$ (sample B) = 162 counts sec^{-1}.

This is equivalent to a pressure of 66 mm.

$\therefore$ number of mmol of $^{36}Cl_2$ present $= \frac{PV}{RT}$

$$= \frac{0.087 \times 498.7}{82.053 \times 297}$$

$$= \underline{1.78 \text{ mmol}}$$

$\therefore$ number of $^{36}Cl_2$ molecules $= 1.78 \times 10^{-3} \times 6.022 \times 10^{23}$

$$= \underline{1.07 \times 10^{21}}$$

weight of $FeCl_3$ (sample B) = 0.7948g

Surface area of $FeCl_3$ (sample B) = 0.22 $m^2 g^{-1}$

$\therefore$ surface area of this sample = 0.175 m^2

$$= \underline{0.175 \times 10^{20} \text{Å}^2}$$

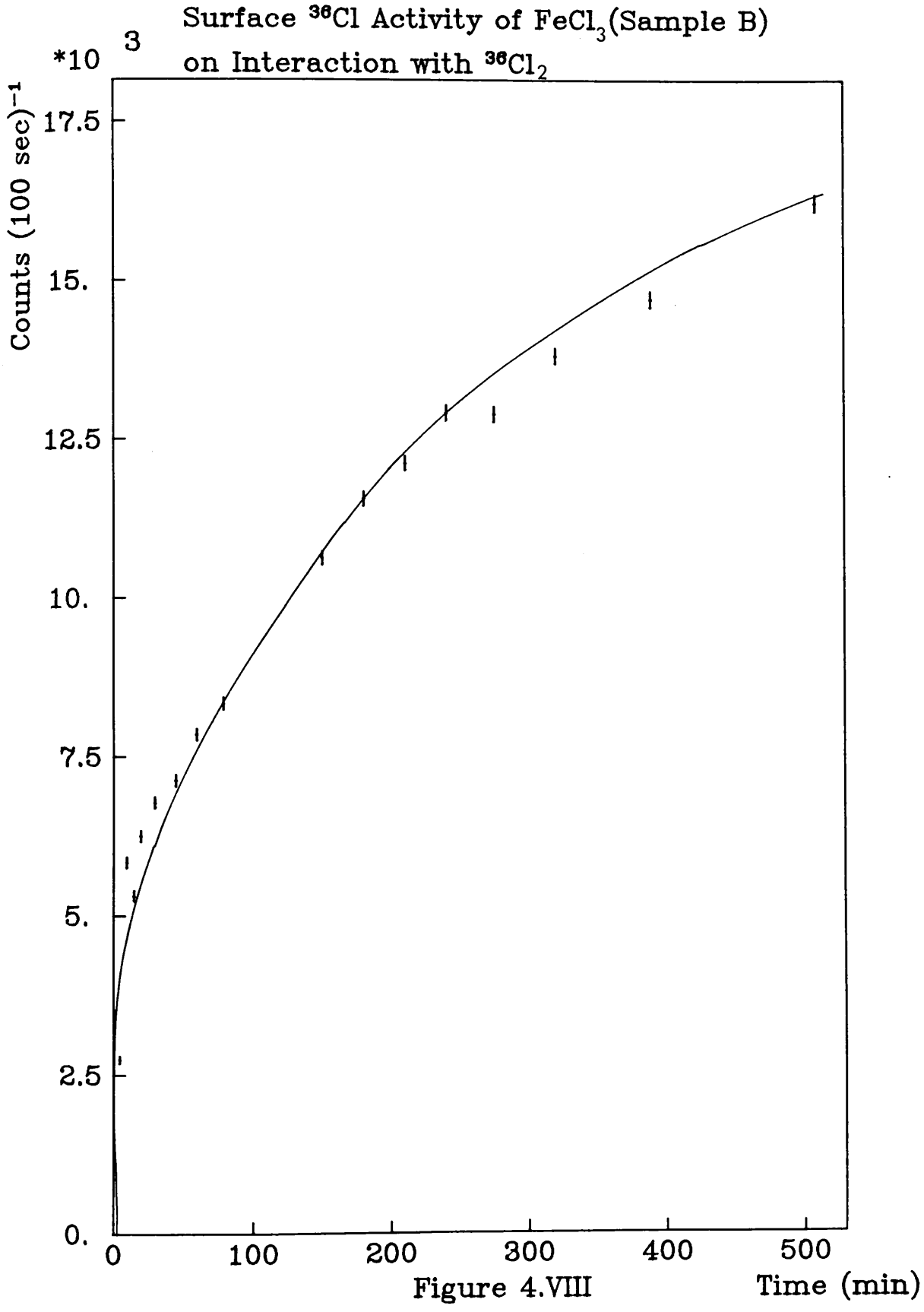


Figure 4.VIII

$93.53 \mathring{A}^2$ corresponds to 3 Fe atoms

$0.175 \times 10^{20} \mathring{A}^2$ corresponds to 5.61×10^{17} Fe atoms.

This implies that 5.61×10^{17} molecules of $^{36}Cl_2$ are required for monolayer coverage. The number of $^{36}Cl_2$ molecules adsorbed by the surface was 1.07×10^{21}, which is more than required for monolayer coverage.

When $^{36}Cl_2$ (0.1853; 2.61 mmol) is admitted to $FeCl_3$ (sample C, commercial anhydrous $FeCl_3$) (0.584g; 3.60 mmol) the same effect as in the two previous reactions is observed and the variation of surface ^{36}Cl activity of $FeCl_3$ with time is shown in Figure 4.IX. The surface activity is unaffected by the removal of $^{36}Cl_2$ from the gas phase and also by the introduction of a fresh sample of inactive Cl_2 or inactive $CHCl_3$. Analysis of the $FeCl_3$ after $CHCl_3$ has been removed indicates that the ratio Fe:Cl is 1:3.0 (Table 4.XXIV) and the $FeCl_3$ is inactive (Table 4.XXV). No ^{36}Cl exchange has occurred but the amount of $^{36}Cl_2$ adsorbed by the $FeCl_3$ has been estimated.

After 8.0h., the surface activity of $FeCl_3$ (sample C) = 220 counts sec^{-1}. This is equivalent to a pressure of 91 mm

$\therefore$ number of mmol of $^{36}Cl_2$ present = $\underline{2.45 \text{ mmol}}$.

$\therefore$ number of $^{36}Cl_2$ molecules = $2.45 \times 10^{-3} \times 6.022 \times 10^{23}$

$= \underline{1.48 \times 10^{21}}$

weight of $FeCl_3$ (sample C) = 0.5846g

surface area of $FeCl_3$ (Sample C) = $0.36 m^2 g^{-1}$

$\therefore$ surface area of this sample = $0.210 m^2$

$= 0.210 \times 10^{20} \mathring{A}^2$

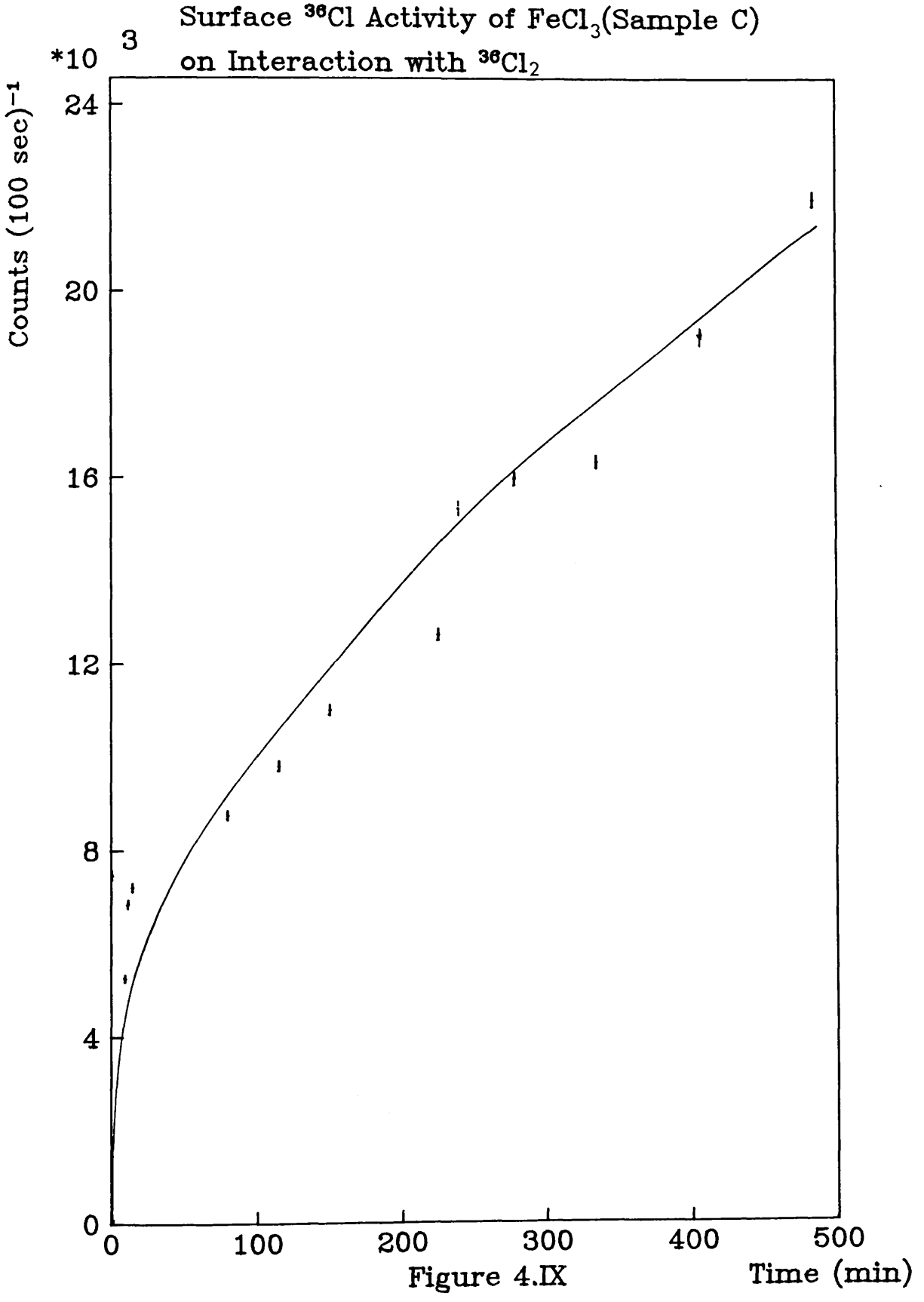

Surface ^{36}Cl Activity of $FeCl_3$(Sample C)
on Interaction with $^{36}Cl_2$
*10 3
Counts (100 sec)$^{-1}$
24
20
16
12
8
4
0
0
100
200
300
400
500
Time (min)

Figure 4.IX

$93.53 \mathring{A}^2$ corresponds to 3 Fe atoms

$0.210 \times 10^{20} \mathring{A}^2$ corresponds to 6.74×10^{17} Fe atoms.

This implies that 6.74×10^{17} molecules of $^{36}Cl_2$ are required for monolayer coverage. The number of $^{36}Cl_2$ molecules adsorbed by the surface was $1.48 \times 10,^{21}$ which is more than is required for monolayer coverage.

4.3.2. EXCHANGE METHOD B

In this method the interaction between $^{36}Cl_2$ and $FeCl_3$ is monitored by removing aliquots of $^{36}Cl_2$ at intervals as described earlier (cf. 2.6.2, Fig. 2.XVIII). 36-Chlorine exchange between $^{36}Cl_2$ and $FeCl_3$ would result in a decrease in the specific activity of the $^{36}Cl_2$ removed and incorporation of activity into the $FeCl_3$.

The initial specific activity of the $^{36}Cl_2$ is determined before $^{36}Cl_2$ (0.4544g; 6.40 mmol) is admitted to $FeCl_3$ (Sample A) (1.5896g; 9.80 mmol). The change in the specific activity of $^{36}Cl_2$ with time, after it is admitted to $FeCl_3$, is shown in Table 4.XXVI. The values obtained are lower than the initial specific activity which suggests that exchange does occur. Analysis of the $FeCl_3$ sample after $^{36}Cl_2$ has been removed indicates that the ratio Fe:Cl is 1:3.0 (Table 4.XXVII) and that $FeCl_3$ is inactive (Table 4.XXVIII). Complete exchange

SPECIFIC ACTIVITIES OF $^{36}Cl_2$ FROM THE INTERACTION OF $FeCl_3$ (SAMPLE A) AND $^{36}Cl_2$.

Specific Activity of $^{36}Cl_2$ counted as $Ag^{36}Cl$. Counts $(5min)^{-1}mg^{-1}$	Time h
604 ± 20	o
387 ± 15	5.5
432 ± 16	30.25
440 ± 16	119

TABLE 4.XXVI

between $^{36}Cl_2$ and $FeCl_3$ would result in ^{36}Cl specific activities of 37 ± 3 counts min^{-1} mg^{-1}. There appears to be a drop between the initial reading for the specific activity of $^{36}Cl_2$ and those taken thereafter but not the corresponding incorporation of activity into $FeCl_3$. This discrepancy cannot be explained by the adsorption of $^{36}Cl_2$ by $FeCl_3$ as this would not alter

ANALYSIS OF $FeCl_3$ SAMPLES FROM EXCHANGE METHOD B

	CHLORINE		IRON	
	% Obtained	% Required for $FeCl_3$	% Obtained	% Required for $FeCl_3$
$FeCl_3$ (Sample A)	57.4	65.6	30.3	34.4
$FeCl_3$ (Sample B)	62.5	65.6	33.1	34.4
$FeCl_3$ (Sample C)	64.0	65.6	33.4	34.4

TABLE 4.XXVII

SPECIFIC ACTIVITIES OF THE REACTIONS FROM EXCHANGE METHOD B

	Specific Activity from Initial Chlorine Counted as $Ag^{36}Cl$. Counts $min^{-1}mg^{-1}$.	Specific Activity from Final Chlorine Counted as $Ag^{36}Cl$. Counts $min^{-1}mg^{-1}$.	Specific Activity From $FeCl_3$. Counted as $Ag^{36}Cl$. Counts $min^{-1}mg^{-1}$.
$FeCl_3$ (Sample A)	121 ± 4	88 ± 3	0.9 ± 0.6
$FeCl_3$ (Sample B)	431 ± 13	396 ± 12	1.4 ± 0.8
$FeCl_3$ (Sample C)	296 ± 9	230 ± 7	1.0 ± 0.7

TABLE 4.XXVIII

the specific activity of the $^{36}Cl_2$. Since the specific activity drops, this implies that some form of inactive chlorine is removed with $^{36}Cl_2$ when it is sampled. This could be caused by trace amounts of water hydrolysing the $FeCl_3$ to a very small extent, producing HCl, followed by slow exchange between HCl + $^{36}Cl_2$. It is known that the half-life of the gas phase exchange reaction between hydrogen chloride and chlorine is very dependent on the amount of water present and under the conditions in this reaction exchange would be slow.[65] Analysis of the $FeCl_3$ sample, however, indicates that the correct ratio Fe:Cl of 1:3.0 is obtained, though the sensitivity of ^{36}Cl is greater than that achieved by conventional wet analysis.

Another explanation for this anomaly is that a systematic error exists in the conversion of ^{36}Cl to $Ag^{36}Cl$ (apart from the uncertainty in the sample weight and the uncertainty inherent in the count.) The results in Table 4.XIV, however, show that there is excellent agreement in the specific activity between the two readings taken, within the limits of the counting and weighing errors, for each sample removed. This suggests that the drop in specific activity is a real effect and is not due to an error in the conversion process. This, however, does not completely rule out the possibility of a systematic error. The significance of the drop is not clear, but it is apparently not due to ^{36}Cl exchange

between $^{36}Cl_2$ and $FeCl_3$.

The change in the specific activity of $^{36}Cl_2$ when $^{36}Cl_2$ (0.1565g; 2.20 mmol) is admitted to $FeCl_3$ (sample B) (0.5790g; 3.57 mmol) is shown in Table 4.XXIX. The specific activity of $^{36}Cl_2$

SPECIFIC ACTIVITIES OF $^{36}Cl_2$ FROM THE INTERACTION OF $FeCl_3$ (SAMPLE B) AND $^{36}Cl_2$.

Specific Activity of $^{36}Cl_2$ Counted as $Ag^{36}Cl$ Counts $(5min)^{-1}mg^{-1}$	Time h
2155 ± 67	0
1802 ± 52	20.33
1790 ± 50	45.25
1831 ± 53	165.83
2130 ± 65	219.25
1980 ± 58	455.33

TABLE 4.XXIX

drops though there is a random fluctuation in the values obtained. Analysis of the $FeCl_3$ sample after $^{36}Cl_2$ has been removed indicates that the ratio Fe:Cl is 1:3.0 (Table 4.XXVII) and that $FeCl_3$ is inactive (Table 4.XXVIII). Complete exchange between $^{36}Cl_2$ and $FeCl_3$ would result in ^{36}Cl specific activities of 125 ± 8 counts min^{-1} mg^{-1}. Although there is a decrease between the initial and final values of $^{36}Cl_2$ specific activities, no activity is incorporated into the $FeCl_3$ sample and, therefore, no exchange occurs.

The change in the specific activity of $^{36}Cl_2$ when $^{36}Cl_2$ (0.2712g; 3.82 mmol) is admitted to $FeCl_3$ (sample C) (0.4641g; 2.86 mmol) is shown in Table 4.XXX. The

SPECIFIC ACTIVITIES OF $^{36}Cl_2$ FROM THE INTERACTION OF $FeCl_3$ (SAMPLE C) AND $^{36}Cl_2$

Specific Activity of $^{36}Cl_2$ Counted as $Ag^{36}Cl$ Counts $(5min)^{-1}mg^{-1}$	Time h
1148 ± 45	0
1309 ± 41	6
1467 ± 44	25.75
1431 ± 43	29.75
1265 ± 39	152.66
1148 ± 37	431.33

TABLE 4.XXX

specific activity of $^{36}Cl_2$ fluctuates but there is a decrease between the initial and final values obtained. Analysis of the $FeCl_3$ sample after $^{36}Cl_2$ has been removed indicates that the ratio Fe:Cl is 1:3.0 (Table XXVII and that the $FeCl_3$ is inactive (Table 4.XXVIII). Complete exchange between $^{36}Cl_2$ and $FeCl_3$ would result in ^{36}Cl specific activities of 61 ± 4 counts $min^{-1}mg^{-1}$. Although there is a decrease between the initial and final values obtained for $^{36}Cl_2$ specific activity, no activity is incorporated into the $FeCl_3$ sample and, therefore, no exchange has occurred.

4.4. DISCUSSION OF THE HETEROGENEOUS REACTIONS

The results from exchange method A, in which the total ^{36}Cl activity is monitored, show that $^{36}Cl_2$ is adsorbed by the glass reaction vessel. The decrease in gas phase activity exhibited when $^{36}Cl_2$ is admitted to all three samples of $FeCl_3$ suggests that either (1) exchange is taking place or (2) that chlorine is adsorbed by the $FeCl_3$. If assumption (1) is correct then analysis of the $FeCl_3$ samples would result in the production of $Ag^{36}Cl$ and ^{36}Cl exchange between $FeCl_3$ and inactive Cl_2 would also be expected. It can be concluded, therefore, that chlorine is merely adsorbed by $FeCl_3$. Comparison of the variation of surface ^{36}Cl activity with time from each of the $FeCl_3$ samples shows

that there is a qualitative correlation between the amount of chlorine adsorbed and the surface area of the $FeCl_3$ sample. (Figure 4.X). Most $^{36}Cl_2$ is adsorbed by $FeCl_3$ (sample C), which has the largest surface area, and least by $FeCl_3$ (sample A), which has the smallest surface area.

Two types of adsorption can take place between a gas and the surface of a solid, chemisorption and physical adsorption. Chemisorption involves the formation of a chemical bond between the gas molecule and the solid surface. A chemisorbed molecule can be either associatively adsorbed or dissociation of the molecule can occur and the species be dissociatively adsorbed by the surface. No chemical bonds are formed between the surface and a physically adsorbed molecule and the forces involved are weak attractive forces similar to van der Waals forces.[67]

If $^{36}Cl_2$ is physically adsorbed by the reaction vessel and the $FeCl_3$, it should be possible to remove the $^{36}Cl_2$ by prolonged pumping of the system at room temperature. Prolonged pumping of the system should not remove a chemisorbed species, which implies that $^{36}Cl_2$ is chemisorbed. $^{36}Cl_2$ could be either associatively or dissociatively adsorbed by the glass. It is known that chloride ion can replace hydroxyl groups on an alumina surface[71] and it is suggested, in an analogous manner, that adsorption occurs by Cl^- or $Cl^{\cdot}$ species replacing hydroxyl groups from the silicate in glass.

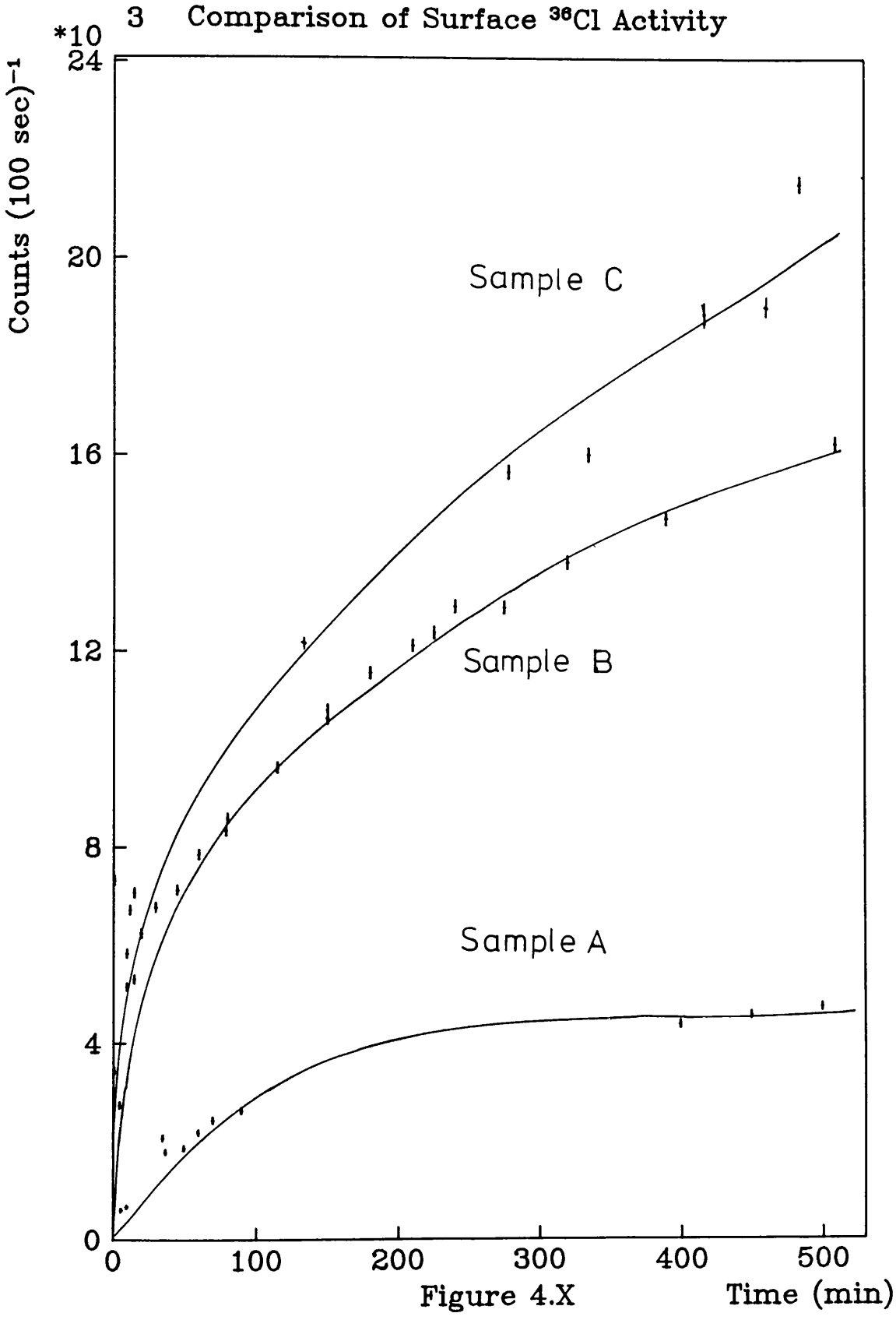

3 Comparison of Surface ^{36}Cl Activity
*10
24
20
16
12
8
4
0
Counts (100 sec)$^{-1}$
Sample C
Sample B
Sample A
0
100
200
300
400
500
Time (min)

Figure 4.X

$^{36}Cl_2$, therefore is dissociatively adsorbed by the glass. If $^{36}Cl_2$ is dissociatively adsorbed by $FeCl_3$, this would lead to randomization of the chloride ions attached to iron and thus to incorporation of activity into $FeCl_3$. No activity is incorporated into $FeCl_3$ which suggests that $^{36}Cl_2$ is associatively adsorbed at the coordinatively unsaturated metal sites (diagram 4.I)

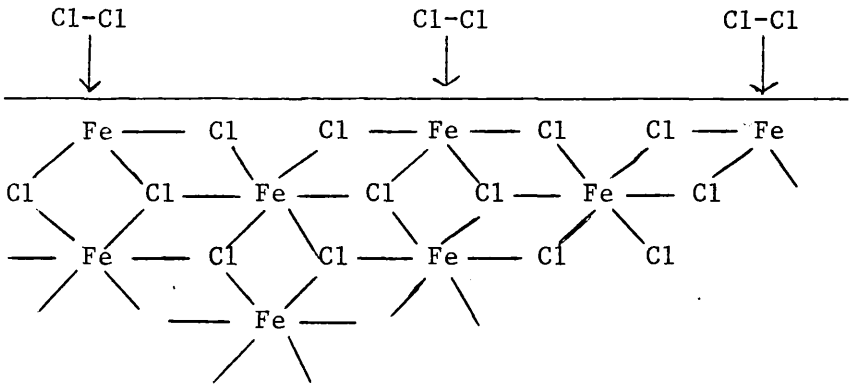


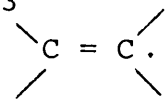
DIAGRAM 4.I

There is no evidence for the adsorbed $^{36}Cl_2$ on hydrolysis of $FeCl_3$ as the ratio Fe:Cl obtained is 1:3.0. This implies that the chemisorbed species is lost during the analysis of $FeCl_3$ which is very probable since this analysis involves dissolving the $FeCl_3$ in acid and boiling the solution (cf.2.3.2).

The results from exchange method B for all three samples of $FeCl_3$ show that there is a decrease between the initial and final activities of $^{36}Cl_2$ but no activity incorporated into $FeCl_3$. Although the significance of this drop is not clear it can be concluded that ^{36}Cl exchange does not occur between $^{36}Cl_2$ and $FeCl_3$.

The chemisorbed species depicted in diagram 4.I is formed due to iron(III) chloride's ability to behave as a Lewis acid. Ethylene reacts with Cl_2 in the presence of iron(III) chloride to give 1,2-dichloroethane (cf. 1.4.1) and it has been suggested that $FeCl_3$ is responsible for the heterolytic cleavage of Cl_2 in the reaction via its Lewis acid activity. (Scheme 1.X).[42] This, however, is inconsistent with the lack of ^{36}Cl exchange between $^{36}Cl_2$ and $FeCl_3$. Benzene can be chlorinated by iron(III) chloride in the presence of chlorine (cf. 1.4.1) though water plays an important role in this reaction. It has been suggested that the role of water is to form '$FeCl_3.H_2O$' which has a greater solubility in benzene than $FeCl_3$ or the higher hydrates.[3] The catalytic effect of anhydrous $AlCl_3$ depends on trace amounts of water or hydrogen halides being present which act as promoters or co-catalysts [40,72] and it has been suggested that this effect is general to Lewis acids. It is extremely difficult to obtain a Lewis acid metal halide in a completely anhydrous state especially in an industrial process. It is probable, therefore, that water is present when ethylene reacts with Cl_2 in the presence of $FeCl_3$ to give 1,2-dichloroethane and that the catalytic ability of $FeCl_3$ is dependent on trace amounts of water which behave as a co-catalyst with $FeCl_3$. In an analogous manner, in the chlorination of benzene by chlorine via an intermediate with $FeCl_3$, water may be necessary not only to increase the solubility of the

catalyst but actually to provide the catalytic species by making iron(III) chloride a more effective Lewis acid.

An alternative explanation from these results is that adsorption of Cl_2 by $FeCl_3$ weakens the Cl-Cl bond which then reacts more readily with  .

In summary, examination of the heterogeneous system between anhydrous $FeCl_3$ and $^{36}Cl_2$ has shown that although $^{36}Cl_2$ is chemisorbed by $FeCl_3$ no exchange occurs. This implies that, under these anhydrous conditions, the Fe(III)-Cl bond is not labile towards Cl_2 and that the suggested role of $FeCl_3$ as a chlorination catalyst is incorrect.

4.5. RESULTS FROM THE HOMOGENEOUS SYSTEM:- IRON(III) CHLORIDE DISSOLVED IN ACETONITRILE.

If water and possibly other Lewis bases can behave as catalyst promoters or co-catalysts with $FeCl_3$ then the presence of a Lewis base should affect Fe^{III}-Cl lability and therefore have an effect on the interaction of $^{36}Cl_2$ with $FeCl_3$. This has been investigated using acetonitrile.

When anhydrous $FeCl_3$ is dissolved in acetonitrile, in an inert atmosphere box at room temperature, a blood-red solution is initially obtained which gradually becomes orange and then pale yellow. The colour change from red to orange takes approximately 24h and the pale yellow stage is achieved in about 14 days. When chlorine is

added to a solution of $FeCl_3$ in acetonitrile, the colour sequence is vastly accelerated. The time taken is dependent on the amount of chlorine added but the sequence of changes is complete within 24h. to 48h.

4.5.1. INTERACTION OF $FeCl_3$ WITH CH_3CN and $^{36}Cl_2$:- RUN I.

This reaction was performed using exchange method B. In this method the interaction between $^{36}Cl_2$ and a solution of $FeCl_3$ in acetonitrile is monitored at intervals by removing aliquots of $^{36}Cl_2$ as described earlier (cf.2.6.2) (Fig. 2.XVIII). If 36-Chlorine exchange occurs the specific activity of $^{36}Cl_2$ will decrease and incorporation of activity into $FeCl_3$ will be observed.

When $^{36}Cl_2$ (0.5886g; 8.29 mmol) is admitted to a solution of $FeCl_3$ in CH_3CN (2.0×10^{-1} mol l^{-1}) the specific activity of $^{36}Cl_2$ drops by approximately one-third after 3h and thereafter remains constant. (Table 4.XXXI) After 20.5 h the amount of $^{36}Cl_2$ removed was too small to count accurately. It became progressively more difficult to remove $^{36}Cl_2$ from this reaction as indicated in Table 4.XXXI by the column headed '%Cl Recovered'. This is defined by

$$\%Cl\ Recovered = \frac{\text{Amount of AgCl obtained x 100}}{\text{Amount AgCl Required for Complete conversion of } ^{36}Cl_2 \text{ to } Ag^{36}Cl}$$

EXCHANGE RESULTS FROM THE INTERACTION OF $FeCl_3$ WITH CH_3CN AND $^{36}Cl_2$:- RUN I.

Sample	Time h	Colour	%Cl Recovered	Activity Counts(5min)$^{-1}$mg^{-1}
Initial $^{36}Cl_2$	0	Red	94.8	858 ± 35
1st. $^{36}Cl_2$	3.25	Red	52.0	561 ± 33
2nd $^{36}Cl_2$	20.5	Orange	31.8	587 ± 25
Remaining Solid	After solvent removed	-	121.1	678 ± 29

TABLE 4.XXXI

The reaction shows the characteristic colour changes and after 30h. the solution is pale yellow. Analysis of the solid sample after the solvent has been removed indicates that the ratio Fe:Cl is 1:3.9 (Table 4.XXXII) and that it is radioactive (Table 4.XXXI). Complete exchange between $^{36}Cl_2$ and $FeCl_3$ would result in $^{36}Cl_2$ specific activities of 726 ± 30 counts (5min)$^{-1}$mg^{-1} for both species.

ANALYSIS OF THE SOLID FROM THE INTERACTION OF $FeCl_3$ WITH CH_3CN AND $^{36}Cl_2$:- RUN I.

	Amount Obtained g	Amount Required for $FeCl_3$ used g
Iron	0.0524	0.0558
Chlorine	0.1285	0.1064

TABLE 4.XXXII

4.5.2. INTERACTION OF $FeCl_3$ WITH CH_3CN AND $^{36}Cl_2$:- RUN II.

When $^{36}Cl_2$ (0.4217g; 5.94 mmol) is admitted to a solution of $FeCl_3$ in CH_3CN (2.0×10^{-1} mol l^{-1}) the specific activity of $^{36}Cl_2$ drops with time (Table 4.XXXIII) until the amount of $^{36}Cl_2$ removed becomes too small to count accurately. This indicates that the pressure of $^{36}Cl_2$ in the reaction vessel is falling. The reaction showed the characteristic

EXCHANGE RESULTS FROM THE INTERACTION OF $FeCl_3$ WITH CH_3CN and $^{36}Cl_2$:- RUN II.

Sample	Time	Colour	%Cl Recovered	Activity Counts(5min)$^{-1}$mg^{-1}
Initial $^{36}Cl_2$	0	Red	98.3	706 ± 36
1st $^{36}Cl_2$	2	Red	80.1	478 ± 30
2nd $^{36}Cl_2$	6.16	Orange	43.7	382 ± 28
Remaining Solid	After solvent removed	-	130.4	642 ± 35

TABLE 4.XXXIII

colour sequence and after 42h. the solution became pale yellow. Analysis of the solid sample after the solvent has been removed indicates that the ratio Fe:Cl is 1:3.9 (Table 4.XXXIV) and that it is active (Table 4.XXXIII).

ANALYSIS OF THE SOLID FROM THE INTERACTION OF $FeCl_3$ WITH CH_3CN AND $^{36}Cl_2$:- RUN II.

	Amount Obtained g	Amount Required for $FeCl_3$ used g
Iron	0.0552	0.0558
Chlorine	0.1380	0.1064

TABLE 4.XXXIV

Complete exchange between $^{36}Cl_2$ and $FeCl_3$ would result in ^{36}Cl specific activities of 564 ± 29. counts $(5min)^{-1}mg^{-1}$ for both species.

The results show that exchange occurs between $^{36}Cl_2$ and $FeCl_3$ in acetonitrile and indicate that this exchange is due to a chemical reaction in which Cl_2 is consumed and which results in a higher ratio Fe:Cl than can be accounted for by $FeCl_3$. This system was more fully investigated to elucidate the chemical reaction.

4.5.3. OXIDATION STATE OF IRON IN THE $FeCl_3|CH_3CN$ AND $FeCl_3|CH_3CN|Cl_2$ SYSTEMS.

The oxidation state of iron was examined at various stages in both the $FeCl_3|CH_3CN$ and the $FeCl_3|CH_3CN|Cl_2$ systems by spectrophotometric analysis (cf. 2.3.3). The iron containing species present in both systems were identified by recording the electronic spectra of the solutions at various times during the reaction.

Spectrophotometric analysis of these solutions show no evidence for the presence of Fe^{II} up to seven days. Thereafter Fe^{II} is present and its concentration remains constant even after four weeks. (Table 4.XXXV). Paradoxically in the $FeCl_3|CH_3CN|Cl_2$ system, Fe^{II} is detected in solution after 20h though the amount of Fe^{II} present is very dependent on the quantity of chlorine

SPECTROPHOTOMETRIC ANALYSIS OF $FeCl_3|CH_3CN$ SYSTEM.

Time	Colour	Fe(II) mg l^{-1}	Total Iron mg l^{-1}
Initial	Red	-	11.4
1h.	Red	-	11.2
20h.	Orange	-	11.2
7d.	Orange	1.7	11.2
4w.	Yellow	3.4	11.1

TABLE 4.XXXV

added to the system. After 20h, the concentration of Fe^{II} in solution decreases and after 44h it is no longer observed. This implies that in the presence of chlorine the reduction of Fe^{III} to Fe^{II} is more rapid than in the $FeCl_3|CH_3CN$ system.

The electronic spectra of the two systems, $FeCl_3|CH_3CN$ and $FeCl_3|CH_3CN|Cl_2$, were recorded over a period of time. Spectroscopic examination of the $FeCl_3|CN_3CN$ system shows the gradual growth of the $Fe(II)(CH_3CN)_6^{2+}$ cation as indicated by a peak at 10900 cm^{-1} and a shoulder at 8500 cm^{-1} which compare favourably with the literature value for this species.[21]

SPECTROPHOTOMETRIC ANALYSIS OF $FeCl_3|CH_3CN|Cl_2$ SYSTEM.

Time	Colour	Cl_2 mmol.	Fe(II) mg l^{-1}	Total Iron mg l^{-1}
1h	Orange	1.60	-	11.3
20h	Yellow	3.01	2.2	11.0
20h	Yellow	3.53	2.8	11.1
44h	Yellow	2.71	-	11.2
4w.	Yellow	3.28	-	11.1

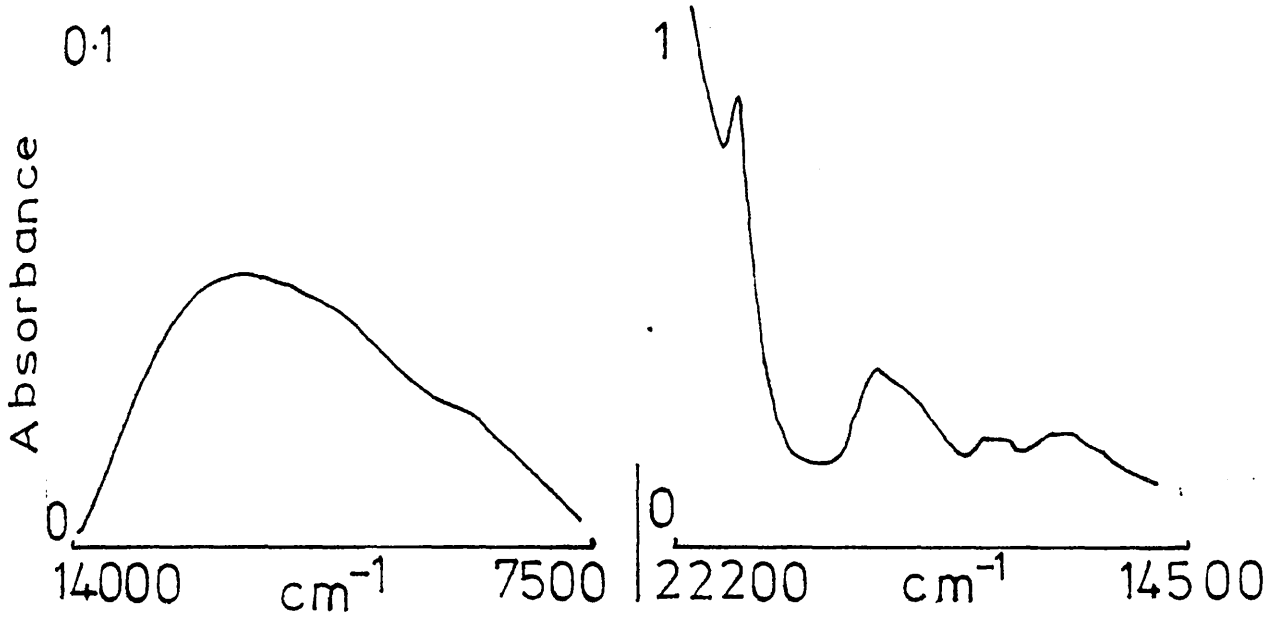
TABLE 4.XXXVI

This peak is due to the ^5D ground state of iron(II) being split by the octahedral field into a lower $^5T_{2g}$ and an upper ^5Eg level and is unsymmetrical as a result of Jahn-Teller distortion of the ^5Eg level. This peak is observed in the $FeCl_3|CH_3CN$ system after seven days and thereafter remains present in these solutions. At the same time, the spectra show the growth of the tetrachloroferrate ion, $FeCl_4^-$ (Table 4.XXXVII and Figure 4.XI).

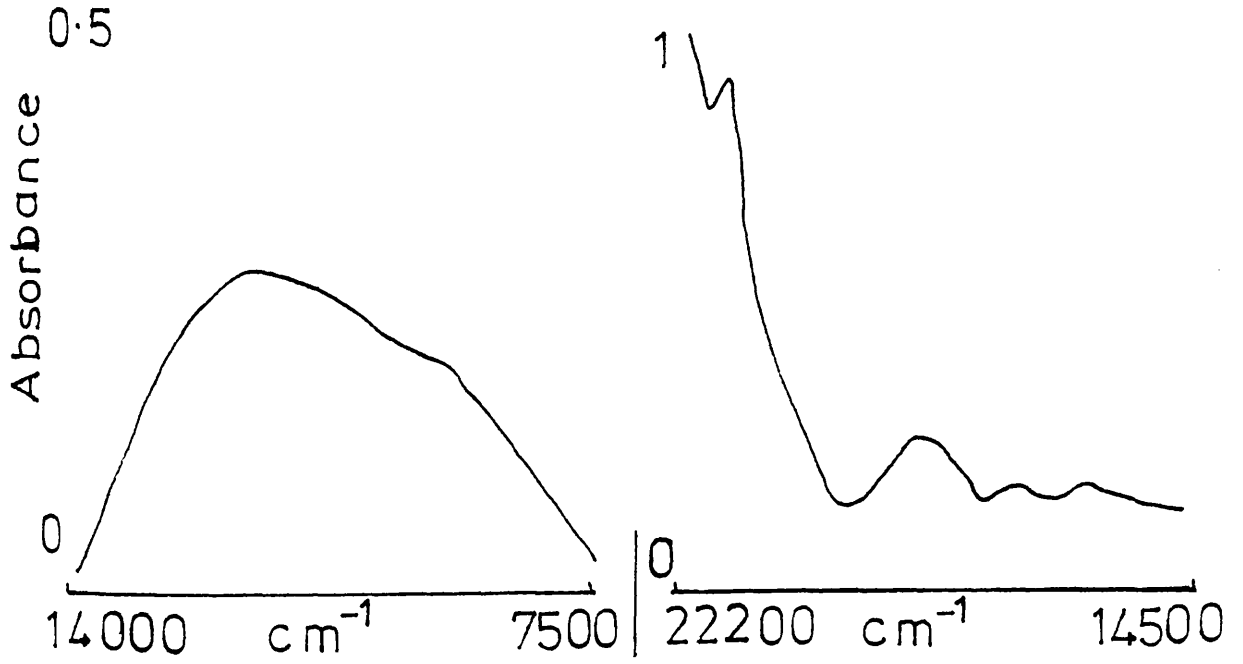
SOLUTION SPECTRUM OF $FeCl_4^-$.

Literature Values [21] of the Solution Spectra of $FeCl_4^-$ cm^{-1}	Observed Values cm^{-1}
48000	Not Observed
41700	41300
37200	37500
32000	31900
27600	27800
22200	22500
19800	Not Observed
18800	18900
16600	16800
16200	16300
14400	14600

TABLE 4.XXXV II



$FeCl_3 | CH_3CN$ System after 1 week



$FeCl_3 | CH_3CN$ System after 3 weeks

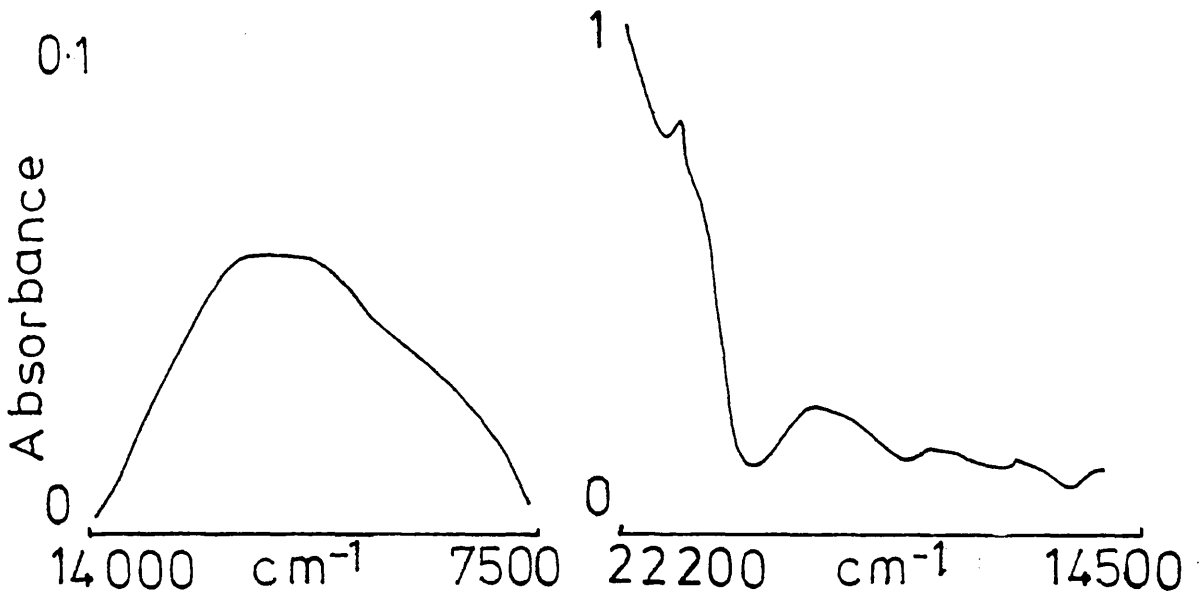
Figure 4XI

In the $FeCl_3|CH_3CN|Cl_2$ system, growth of $Fe(CH_3CN)_6^{2+}$ is observed during the first twenty hours but thereafter it decays until after 44h. it is no longer observable. Simultaneously the spectra show the growth of the $FeCl_4^-$ ion and after 48h. this is the only iron-containing species observed in solution. (Figure 4.XII).

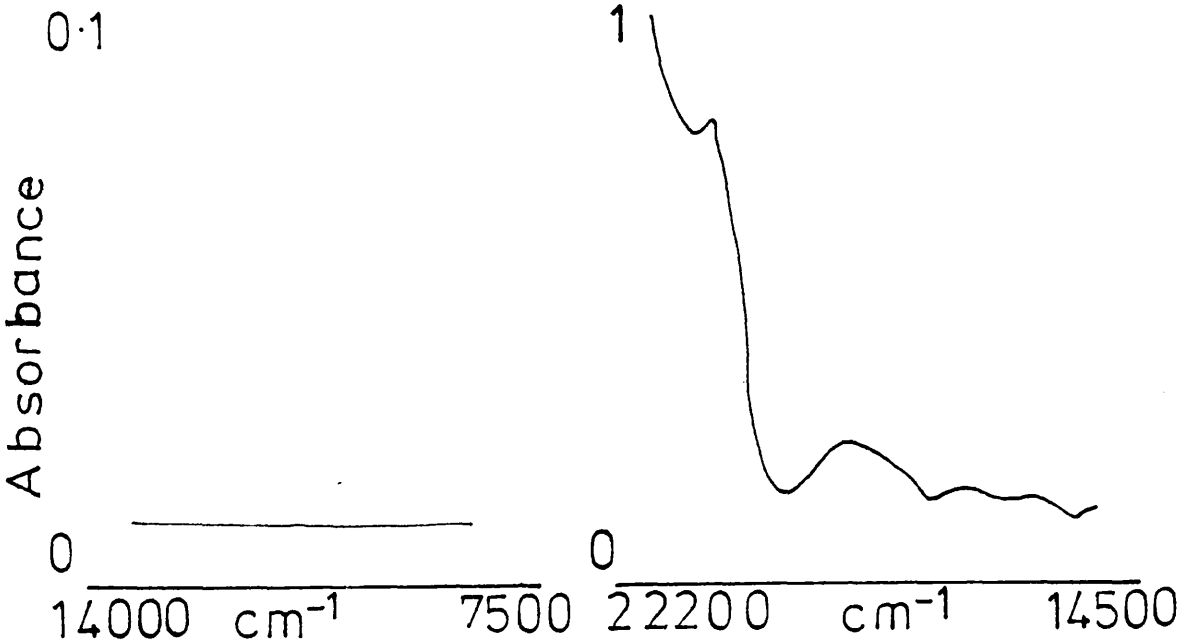
4.5.4. CHLORINATION OF THE SOLVENT.

The formation of Fe^{II} in these solutions suggests that chlorination of the solvent occurs with the concomitant evolution of HCl. The solvents from the three systems, $CH_3CN|Cl_2$, $FeCl_3|CH_3CN$ and $FeCl_3|CH_3CN|Cl_2$, were examined by GLC for the presence of monochloroacetonitrile and trichloroacetonitrile to establish the extent of chlorination.

The systems were prepared under comparable conditions at room temperature and examined after 20h. In two cases monochloroacetonitrile is formed (Table 4.XXXVIII) but no trichloroacetonitrile was observed in any solution.



$FeCl_3|CH_3CN|Cl_2$ System after 20 h.



$FeCl_3|CH_3CN|Cl_2$ System after 48 h.

Figure 4XII

GLC. ANALYSIS OF REACTION SOLUTIONS.

	$\frac{\text{Vol.}CH_2ClCN}{\text{Vol.}CH_3CN} \times 100$	CH_2ClCN Mol l^{-1}
$CH_3CN\|Cl_2$	0.016	0.003
$FeCl_3\|CH_3CN$	-	-
$FeCl_3\|CH_3CN\|Cl_2$	0.290	0.046

TABLE 4.XXXVIII

Under these conditions, no CH_2ClCN was detected in the $FeCl_3|CH_3CN$ system. In the $FeCl_3|CH_3CN|Cl_2$ system, chlorination of the solvent is significant and far greater than in the absence of $FeCl_3$.

The effect of varying the $FeCl_3$:Cl_2 ratio on the extent of chlorination is shown in Table 4.XXXIX . In these experiments the solutions were allowed to react at 298K for 7 days. Both mono- and trichloroacetonitrile are formed in these solutions and as more chlorine is added the amount of CH_2ClCN decreases but

EXTENT OF SOLVENT CHLORINATION FROM THE $FeCl_3|CH_3CN|Cl_2$ SYSTEM.

Cl_2 mmol.	CH_2ClCN $\frac{vol.CH_2ClCN}{vol.CH_3CN}$ X100	CH_2ClCN mol l^{-1}	CCl_3CN $\frac{vol.CCl_3CN}{vol.CH_3CN}$ x100	CCl_3CN mol l^{-1}
0.915	0.392	0.062	0.160	0.016
2.14	0.532	0.084	0.112	0.011
2.99	0.494	0.078	0.332	0.033
4.91	0.418	0.066	0.405	0.040
6.40	0.046	0.007	0.900	0.090

CONCENTRATION OF $FeCl_3$ IN CH_3CN = 2.0×10^{-2} mol l^{-1}

TABLE 4.XXXIX

the amount of CCl_3CN present increases. These results indicate that the extent of chlorination is dependent on the amount of chlorine added.

It has been shown that $Fe(CH_3CN)_6^{2+}$ is oxidised by Cl_2 in CH_3CN to give $FeCl_4^-$ as the only iron-containing product.[73] The solvent from this was examined to determine the extent of chlorination which occurs when the $[Fe(CH_3CN)_6][PF_6]_2$:Cl_2 ratio is varied. (Table 4.XL). Both mono- and trichloroacetonitrile are formed in these solutions and as more chlorine is added the amount of CH_2ClCN decreases but the amount of CCl_3CN present increases.

4.6. DISCUSSION OF THE HOMOGENEOUS SYSTEM:- IRON(III) CHLORIDE DISSOLVED IN ACETONITRILE.

When $^{36}Cl_2$ is added to a solution of $FeCl_3$ in acetonitrile, ^{36}Cl exchange takes place. This is indicated by a decrease in the specific activity of the $^{36}Cl_2$ and the incorporation of activity into $FeCl_3$. Under the experimental conditions used, the specific activity of $^{36}Cl_2$ has decreased by ca 30% after 3h. These results were obtained using exchange method B which, due to the results discussed in section 4.3.2, makes this figure of

EXTENT OF SOLVENT CHLORINATION FROM THE $[Fe(CH_3CN)_6]^{2+}$ $|CH_3CN|Cl_2$ SYSTEM.

Cl_2 mmol.	CH_2ClCN		CCl_3CN	
	$\frac{vol.CH_2ClCN}{vol.CH_3CN}$ x100	mol l^{-1}	$\frac{vol.CCl_3CN}{Vol.CH_3CN}$ x100	mol l^{-1}
1.15	0.725	0.115	-	-
2.53	0.863	0.136	-	-
2.86	0.906	0.143	-	-
4.17	0.472	0.075	0.080	0.008
14.30	0.090	0.014	0.335	0.033

CONCENTRATION OF $(PF_6)_2Fe(CH_3CN)_6$ IN CH_3CN = 2.0×10^{-2} mol l^{-1}

TABLE 4.XL

30% slightly suspect. Analysis of $FeCl_3$, after the removal of the solvent, indicates that the ratio Fe:Cl is 1:3.9 which could result from the almost complete conversion of $FeCl_3$ to the tetrachloroferrate ion. It appears that the ^{36}Cl exchange observed is the result of a chemical reaction.

The reaction is characterized by the colour changes red → orange → pale yellow. The coordination model put forward by Drago et. al. [6,7,8] and shown in scheme 1.II suggests that when iron(III) chloride is dissolved in acetonitrile, complexation and solvolysis occur. It has been suggested that the species formed are $[Fe(CH_3CN)_4Cl_2]^+$ and $FeCl_4^-$.[74] It is also known that in acetonitrile, partial reduction of the $FeCl_3$ occurs and after a week $[Fe^{II}(CH_3CN)_6][Fe^{III}Cl_4]_2$ can be isolated from a pale yellow solution.[18] A crystal structure of this compound has been obtained and found to contain two tetrahedrons $(Fe^{III}Cl_4)^-$ and one octahedron $[Fe^{II}(CH_3CN)_6]^{2+}$.[75] It has been suggested that the presence of water and light play an important role in the reduction of $FeCl_3$ by nitriles. It was found when $FeCl_3$ is dissolved in a nitrile, RCN, under rigorously anhydrous conditions and protected from light that highly unstable red crystals

were formed. These crystals decomposed on exposure to light, heat and traces of moisture. Chemical analysis of the crystals showed that the chlorine to iron ratio was 2.83±0.09 and that the ligand to iron ratio was 1.84. This data is compatible with the compound $[Fe(CH_3CN)_4Cl_2][FeCl_4]$. An X-ray diffraction study was carried out on the crystals obtained from $FeCl_3$ dissolved in C_2H_5CN and the lattice contained eight $FeCl_4^-$ tetrahedra for every four $[Fe(C_2H_5CN)_5Cl]^{2+}$ octahedra.[75] This structure agreed with the chemical analysis which showed that the ligand to iron ratio was 1.7.[76] These results imply that the partial reduction of $FeCl_3$ in acetonitrile may be catalysed by trace amounts of water.

From these various studies it appears that the colour changes observed are due to the formation of different species in solution. In an attempt to relate the colour changes observed with the species formed, the oxidation state of the iron was examined. The results show that after a week Fe^{II} is detected in solutions of $FeCl_3$ in CH_3CN and that the Fe^{II} concentration increases until one third of the iron is present as Fe^{II}. Electronic spectra indicate that this species is $Fe^{II}(CH_3CN)_6^{2+}$ and that the rest of the iron is present as $FeCl_4^-$. At this stage the solution is pale yellow and since $Fe^{II}(CH_3CN)_6^{2+}$ is effectively colourless, $FeCl_4^-$ must be responsible for this yellow colour.

The sequence of colour changes can, therefore, be explained as follows. Complexation occurs between $FeCl_3$ and CH_3CN giving rise to the red colour observed initially. Solvolysis then occurs and, as acetonitrile is a weak donor of moderate solvating ability, $[Fe(CH_3CN)_4Cl_2]^+$ and $FeCl_4^-$ are gradually formed in solution. The $[Fe(CH_3CN)_4Cl_2]^+$ cation can dissociate to give $[Fe(CH_3CN)_5Cl]^{2+}$ (scheme 4.I) but, due to acetonitrile's solvating properties, this equilibrium lies to the left. It has

$$[Fe(CH_3CN)_4Cl_2]^+ \rightleftharpoons [Fe(CH_3CN)_5Cl]^{2+}$$

Scheme 4.I.

been shown that $[Fe(CH_3CN)_5Cl]^{2+}$ does not dissociate to give $[Fe(CH_3CN)_6]^{3+}$, as $[Fe(CH_3CN)_6]^{3+}$ is too powerful an oxidising agent to exist under these conditions.[73] The solvated iron(III) species, $[Fe(CH_3CN)_4Cl_2]^+$ formed in solution is then slowly reduced and after a week $[Fe(CH_3CN)_6]^{2+}$ is present in solution. (scheme 4.II)

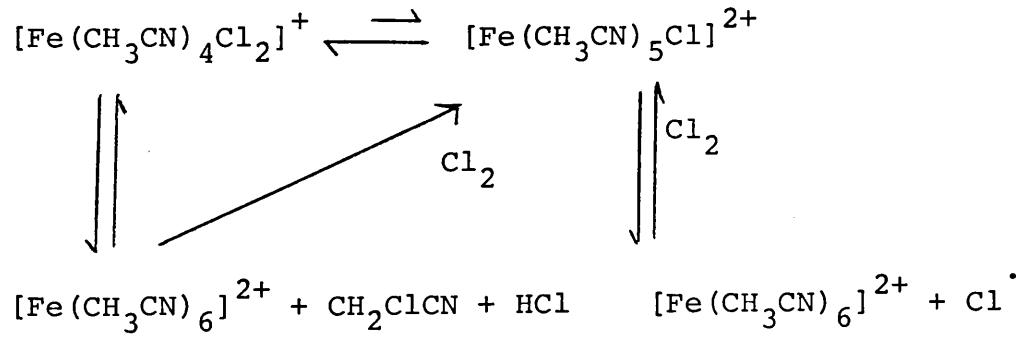
$$[Fe(CH_3CN)_4Cl_2]^+ \rightleftharpoons [Fe(CH_3CN)_6]^{2+} + Cl^{\cdot} + Cl^-$$

Scheme 4.II

Although every effort was taken to exclude trace quantities of water in the present work, this step may be catalysed by trace amounts of water. Reduction of the Fe^{III} species results in $[Fe(CH_3CN)_6]^{2+}$ and $FeCl_4^-$ being present in solution after a week. Chemical analysis of iron's oxidation state confirms that the ratio $Fe^{II}:Fe^{III}$ is 1:2.

When $FeCl_3$ is dissolved in CH_3CN in the presence of

chlorine, Fe^{II} is detected in solution after only 20h. and at this stage ca 20% of the iron is present as Fe^{II}, although the exact amount is dependent on the amount of chlorine added to the system. Thereafter, the concentration of Fe^{II} decreases until after 44h. it can no longer be detected. Electronic spectra identified the Fe^{II} species as $[Fe(CH_3CN)_6]^{2+}$. In contrast, the concentration of $FeCl_4^-$ increases throughout the reaction and after 44h this is the only species observed. Paradoxically in the presence of an oxidising agent, Fe^{II} is detected earlier in solution. A possible explanation for these results is that, after complexation and solvolysis occurs to give $[Fe(CH_3CN)_4Cl_2]^+$ and $FeCl_4^-$, the cationic species is reduced and, in the presence of chlorine, oxidised to the $[Fe(CH_3CN)_5Cl]^{2+}$ ion. The $[Fe(CH_3CN)_5Cl]^{2+}$ ion is immediately reduced giving $[Fe(CH_3CN)_6]^{2+}$. (Scheme 4.III)



Scheme 4.III

Presuming that $[Fe(CH_3CN)_5Cl]^{2+}$ is reduced more quickly than $[Fe(CH_3CN)_4Cl_2]^+$ and that the reduction is

more rapid than the oxidation, then this will lead to a more rapid build-up of the Fe^{II} species in solution. In this system, however, after 44h all the iron is present as $FeCl_4^-$. In the reduction of the cationic iron(III) species to $Fe(CH_3CN)_6^{2+}$ and in the latters oxidation by chlorine, chlorination of the solvent must occur with the concomitant evolution of HCl. Free HCl is not detected in any of the systems studied, that is $FeCl_3|CH_3CN$, $CH_3CN|Cl_2$ and $FeCl_3|CH_3CN|Cl_2$. This implies that HCl is consumed in these reactions. There are a number of ways in which it has been suggested that HCl can react with acetonitrile. These are a) formation of the solvent adduct $CH_3CN.xHCl$;[77] b) formation of the acetamido dichloride[78] (Fig. 4.XIIIA) c) addition across the C≡N bond to give the chloroacetiminium chloride[79] (Fig. 4.XIIIB) and d) formation of the hydrogen dichloride ion [80,81,82] (Fig. 4.XIIIC).

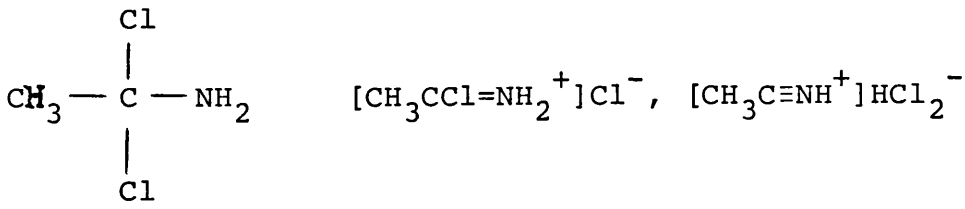


Fig. 4.XIII

The infrared spectra of the three systems, $FeCl_3|CH_3CN$, $CH_3CN|Cl_2$ and $FeCl_3|CH_3CN|Cl_2$, were recorded

and examined in an attempt to match the bands obtained to those assigned for these structures. This, however, was not possible as very little could be discerned from these spectra apart from the CH_3CN bands. As the amount of HCl which would be produced is small, then the concentration of the product in solution may be too small to observe. If, however, the HCl had added across the C≡N bond then it is expected that some of the bands, for example the strong C-Cl stretching mode at 750 cm^{-1} would have been observed. If the hydrogen dichloride ion species had been formed then it is highly unlikely that any bands due to this species would be observed as the hydrogen dichloride ion would be strongly hydrogen bonded in solution. In the $FeCl_3|CH_3CN|Cl_2$ system, there is another possibility in which the HCl reacts with a solvated iron(III) species $[FeCl_x(CH_3CN)_{6-x}]^{(3-x)+}$ to produce $FeCl_4^-$. (Scheme 4.IV)

$$[FeCl_x(CH_3CN)_{6-x}]^{(3-x)+} + HCl \rightarrow FeCl_4^- + CH_3CNH^{\oplus}$$

Scheme 4.IV

Thus the total conversion of all the iron species to the tetrachloroferrate ion in the $FeCl_3|CH_3CN|Cl_2$ system can be explained as follows. The redox reaction between the Fe^{II} and Fe^{III} species results in chlorination of the solvent and the production of HCl. The HCl produced reacts with the cationic Fe^{III} species to give the redox inactive $FeCl_4^-$, thus breaking the redox

cycle. The overall reaction in this system is shown in 4.III.

$$FeCl_3 + CH_3CN + Cl_2 \rightarrow FeCl_4^- + CH_2ClCN + H^+(solv.) \quad \text{....4.III}$$

Separate experiments have established that $[Fe(CH_3CN)_6]^{2+}$ is oxidised by Cl_2 in acetonitrile to give $FeCl_4^-$ as the only iron-containing product.[73] The $[Fe(CH_3CN)_6]^{2+}$ is oxidised to give $[Fe(CH_3CN)_5Cl]^{2+}$ which is immediately reduced back to the Fe^{II} species thus resulting in a redox cycle. This redox cycle results in chlorination of the solvent with the concomitant evolution of HCl. The HCl produced breaks the redox catalytic cycle by reacting with the cationic Fe^{III} species to form the redox inactive $FeCl_4^-$. This experiment is important as it indicates that the catalytic redox cycle is initiated by either a cationic Fe^{II} or Fe^{III} species.

When $FeCl_3$ is dissolved in CH_3CN, the ratio of Fe^{II} to Fe^{III} is 1:2. It has also been reported that where iron(III) chloride is dissolved in acrylonitrile, one-third of the iron is reduced to iron(II) accompanied by chlorination of the solvent.[83] Although the ratio Fe^{II}:Fe^{III} has been found to be 1:2 in a number of reactions, no satisfactory explanation for this has been given. The ratio found for Fe^{II}:Fe^{III} can be explained by the reactions shown in scheme 4.V.

$$[(FeCl_3)_xCH_3CN_y] \rightleftharpoons 3[Fe(CH_3CN)_4Cl_2]^+ + 3FeCl_4^-$$

$$2[Fe(CH_3CN)_4Cl_2]^+ \rightleftharpoons 2[Fe(CH_3CN)_6]^{2+} + CH_2ClCN + HCl + 2Cl^-$$

$$[Fe(CH_3CN)_4Cl_2]^+ + 2HCl \rightleftharpoons FeCl_4^- + 2CH_3CNH^{\oplus}$$

Scheme 4.V

Hathaway and Holah found when iron is reacted with chlorine in acetonitrile that the product formed is $[Fe(CH_3CN)_6][FeCl_4]_2$.[21] In this reaction, iron has been oxidised to form a mixed oxidation state complex with a third of the iron present as Fe^{II} and two-thirds present as Fe^{III}. The authors expressed surprise that chlorine, which is a powerful oxidising agent, did not oxidise all the iron(II) to iron(III). They explained this by suggesting that the tetrachloroferrate formed is sufficiently stable to prevent complete oxidation of iron to iron(III). As a result of the present work an alternative explanation is offered. It is known[73] that an iron(III) species is not stable when octahedrally surrounded by acetonitrile ligands and that an acetonitrile ligated iron(III) species can only exist when stabilized by ligands such as chlorine. $[Fe(CH_3CN)_4Cl_2]^+$ and $FeCl_4^-$ will, therefore, be formed in solution and will react as shown in scheme 4.V to achieve the ratio of $1Fe^{II}:2Fe^{III}$. Results show that when chlorine is added to a solution of $FeCl_3$ in CH_3CN all the iron is present as $FeCl_4^-$.

The mixed oxidation state compound formed from the reaction of iron with chlorine in acetonitrile is a concentration effect caused by only enough chlorine being added to form $[Fe(CH_3CN)_4Cl_2]^+$ and $FeCl_4^-$. If more Cl_2 had been added all the iron species would have been converted to $FeCl_4^-$ as previously discussed.

In the $FeCl_3|CH_3CN|Cl_2$ system and in other reports of reduction or partial reduction of metal chlorides by acetonitrile, the reduction of the metal ion must result in chlorination of the solvent and evolution of HCl. Although the final product from the reaction of VCl_4 and excess acetonitrile has been characterized and the formation of trichloroacetonitrile proposed (scheme 1.III), the initial stages of this reaction have not been elucidated. As the formation of trichloro-acetonitrile is necessary in this mechanism, it is reasonable to assume that monochloroacetonitrile is a precursor. As chlorination of the solvent occurs in the $CH_3CN|Cl_2$ system, this suggests that a free-radical mechanism is involved. In the $FeCl_3|CH_3CN|Cl_2$ system, substantial chlorination occurs, the extent of which is dependent on the amount of chlorine added, and both CH_2ClCN and CCl_3CN are formed in solution. As more chlorine is added the concentration of CCl_3CN increases but that of CH_2ClCN decreases. It has been observed that treatment of acetonitrile by hydrogen chloride increases the rate of chlorination.[84] If the first step in the chlorination is the attack of the

solvent by a free radical, $Cl^{\cdot}$, leading to the formation of CH_2ClCN then HCl will be liberated. The HCl liberated adds to the partly chlorinated nitrile forming a nitrilium salt which is more readily chlorinated than acetonitrile.[84] (Scheme 4.VI).

$$Cl^{\cdot} + CH_3CN \rightarrow {}^{\cdot}CH_2CN + HCl$$
$${}^{\cdot}CH_2CN + Cl_2 \rightarrow CH_2ClCN + Cl^{\cdot}$$
$$CH_2ClCN + HCl \rightarrow (CH_2ClCNH)^{+}Cl^{-}$$
$$(CH_2ClCNH)^{+}Cl^{-} + Cl_2 \rightarrow (CHCl_2CNH)^{+}Cl^{-} + HCl$$
$$(CHCl_2CNH)^{+}Cl^{-} + Cl_2 \rightarrow (CCl_3CNH)^{+}Cl^{-} + HCl$$
$$(CCl_3CNH)^{+}Cl^{-} \rightarrow CCl_3CN + HCl$$

Scheme 4.VI

The increase in the CCl_3CN concentration and the decrease in the CH_2ClCN concentration as more Cl_2 is added is explained by the preferential chlorination of the nitrilium salt. The number of times the redox cycle has been repeated is estimated by examining the extent of chlorination which occurs when varying amounts of chlorine were added to $FeCl_3$ in CH_3CN. This is shown in the following calculation.

Each 5ml solution contains 0.1 mmol of $FeCl_3$, therefore

$$0.1 \text{ mmol } FeCl_3 + nCH_3CN \rightleftharpoons FeCl_3(MeCN)_n \rightleftharpoons 0.05 \text{ mmol } [Fe(CH_3CN)_4Cl_2]^{+} + 0.05 \text{ mmol } FeCl_4^{-}$$

$$0.05 \text{ mmol } [Fe(CH_3CN)_4Cl_2]^{+} \rightleftharpoons 0.05 \text{ mmol } [Fe(CH_3CN)_6]^{2+} + 0.025 \text{ mmol } CH_2ClCN + 0.025 \text{ mmol } HCl + Cl^{-}$$

$$0.05 \text{ mmol } [Fe(CH_3CN)_6]^{2+} + Cl_2 \rightleftharpoons 0.05 \text{ mmol } [Fe(CH_3CN)_5Cl]^{2+} + 0.025 \text{ mmol } CH_2ClCN + 0.025 \text{ mmol HCl}$$

$$0.05 \text{ mmol } [Fe(CH_3CN)_5Cl]^{2+} \rightleftharpoons 0.05 \text{ mmol } [Fe(CH_3CN)_6]^{2+} + 0.025 \text{ mmol } CH_2ClCN + 0.025 \text{ mmol HCl.}$$

Assuming complete conversion in every stage of the reaction, then the first cycle produces 0.075 mmol CH_2ClCN and thereafter each cycle produces 0.05 mmol CH_2ClCN.

When 0.915 mmol Cl_2 was added to a solution of $FeCl_3$ in CH_3CN it produced 0.062 mol l^{-1} CH_2ClCN and 0.016 mol l^{-1} CCl_3CN. Therefore in 5 ml, there were 0.31 mmol CH_2ClCN and 0.08 mmol CCl_3CN which in total is equivalent to the production of 0.55 mmol CH_2ClCN. This would require the redox cycle to be repeated a minimum of 10 times.

6.40 mmol Cl_2 produces 0.007 mol l^{-1} CH_2ClCN

$\Rightarrow$ 0.035 mmol in 5 ml.

and 0.090 mol l^{-1} CCl_3CN

$\Rightarrow$ 0.45 mmol in 5ml

$\equiv$ 1.35 mmol of CH_2ClCN in 5ml

$\therefore$ The total amount of CH_2ClCN produced = 1.385 mmol.

This would require the redox cycle to be repeated a minimum of 27 times.

These results, therefore, confirm the formation of CH_2ClCN and CCl_3CN in the initial stages of the reaction.

In the absence of chlorine, that is in the $FeCl_3|CH_3CN$ system, no chlorination was observed. This solvent, however, was examined only after 20h and chlorination of the solvent would not be expected until some Fe^{II} had been formed in solution which takes about a week under the conditions used.

An overall reaction mechanism for iron(III) chloride dissolved in acetonitrile in the presence of chlorine is given in scheme 4.VII. In this initial complexation and solvolysis occurs between $FeCl_3$ and CH_3CN forming $[Fe(CH_3CN)_4Cl_2]^+$ and $FeCl_4^-$. The $[Fe(CH_3CN)_4Cl_2]^+$ ion is reduced giving the iron(II) species, $[Fe(CH_3CN)_6]^{2+}$ which is oxidised by the chlorine giving $[Fe(CH_3CN)_5Cl]^{2+}$. The $[Fe(CH_3CN)_5Cl]^{2+}$ ion is also reduced to the iron(II) species, thus forming a redox cycle. The redox cycle can be regarded as catalytic since it results in chlorination of the solvent. The lifetime of the cycle is limited due to the production of HCl which reacts with the cationic iron(III) species leading to the redox inactive $FeCl_4^-$. This redox cycle is also formed when $[Fe(CH_3CN)_6][PF_6]_2$ is dissolved in acetonitrile in the presence of chlorine and this again results in chlorination of the solvent. This shows that either the cationic Fe^{II} species or the cationic Fe^{III} species can initiate the redox cycle which leads to the chlorination of the solvent.

The ^{36}Cl exchange observed when $^{36}Cl_2$ is added to a solution of $FeCl_3$ in acetonitrile is a result of the chemical reaction shown in scheme 4.VII. It can therefore be concluded that in this reaction, the presence of the

Lewis base has a labilising effect on the Fe^{III}-Cl bond and that chlorination of the solvent is a result of the redox cycle.

$$FeCl_3 + nCH_3CN \rightleftharpoons [FeCl_3(CH_3CN)_n] \rightleftharpoons [Fe(CH_3CN)_4Cl_2]^+ + FeCl_4^-$$

$$[Fe(CH_3CN)_4Cl_2]^+ \rightleftharpoons [Fe(CH_3CN)_6]^{2+} + \tfrac{1}{2}CH_2ClCN + \tfrac{1}{2}HCl + Cl^-$$

$$[Fe(CH_3CN)_6]^{2+} + Cl_2 \rightarrow [Fe(CH_3CN)_5Cl]^{2+} + \tfrac{1}{2}CH_2ClCN + \tfrac{1}{2}HCl$$

$$[Fe(CH_3CN)_5Cl]^{2+} \rightleftharpoons [Fe(CH_3CN)_6]^{2+} + \tfrac{1}{2}CH_2ClCN + \tfrac{1}{2}HCl$$

$$[FeCl_x(CH_3CN)_{6-x}]^{(3-x)+} + HCl \rightarrow FeCl_4^- + CH_3CNH^{\oplus}$$

Scheme 4.VII

CHAPTER FIVE

CHAPTER 5

INTERACTION OF IRON(III) CHLORIDE WITH HYDROGEN CHLORIDE.

Iron(III) chloride is an efficient hydrochlorination catalyst and is used industrially for the addition of HCl to vinyl chloride, vinylidene chloride and 1,2 dichloro-ethylene (cf. 1.4.3). Reactions are often performed in which the iron(III) chloride has been dissolved in a donor solvent and it has been postulated that the reactions occur via the ionization of HCl. (eq. 5.1)

$$FeCl_3 + HCl \rightleftharpoons H^+(\text{solvated})\ FeCl_4^- \quad \ldots\ldots\ldots\ldots (Eq.\ 5.i)$$

If this is correct then it is expected that exchange will occur between $H^{36}Cl$ and $FeCl_3$. The equilibrium shown in Equation 5.1 will be effected by the presence of water which could react with $FeCl_3$ to give $H_3O^+FeCl_4^-$ and thus lead to ^{36}Cl exchange. It has been shown by a study of the iron(III) chloride - water phase diagram that four hydrates exist; $FeCl_3.2H_2O$, $FeCl_3.2\frac{1}{2}H_2O$, $FeCl_3.3\frac{1}{2}H_2O$ and $FeCl_3.6H_2O$.[85] The structures of these hydrates have been determined and are shown in Table 5.I. The production

STRUCTURE OF $FeCl_3$ HYDRATES

Compound	Structure	Method of Determination
$FeCl_3.2H_2O$	trans-$[FeCl_2(H_2O)_4]^+[FeCl_4]^-$	IR[86], Mössbauer[87]
$FeCl_3.2\frac{1}{2}H_2O$	cis$[FeCl_2(H_2O)_4]^+[FeCl_4]^-.H_2O$	X-ray[36], Mössbauer[87]
$FeCl_3.3\frac{1}{2}H_2O$	cis$[FeCl_2(H_2O)_4]^+[FeCl_4]^-.3H_2O$	Mössbauer[87]
$FeCl_3.6H_2O$	trans$[FeCl_2(H_2O)_4]^+Cl^-.2H_2O$	X-ray[35], Mössbauer[87]

TABLE 5.1

of $FeCl_4^-$ and Cl^- in the formation of these hydrates is expected to have an effect on ^{36}Cl exchange and the exchange could involve $[Fe(H_2O)_4Cl_2]^+$, $FeCl_4^-$ or Cl^- depending on the amount of water present.

To develop a better understanding of hydrochlorination reactions, experiments were carried out between $FeCl_3$ and $H^{36}Cl$, to ascertain the conditions under which exchange occurs.

5.1. Experimental

These reactions were all monitored by Exchange method A. In this method the interaction between $H^{36}Cl$ and $FeCl_3$ is monitored by two GM tubes contained in an evacuable counting vessel which has been described earlier (cf. 2.6.1. Fig. 2.XV). ^{36}Cl exchange between $H^{36}Cl$ and $FeCl_3$ or adsorption of $H^{36}Cl$ by the solid results in an increased count from the tube monitoring the solid plus gas and a decreased count from that monitoring the gas phase only.

5.1.1. Interaction of $H^{36}Cl$ with the glass exchange vessel.

A sample of $H^{36}Cl$ was purified by the procedure given in 2.4.1. and was colourless at 77K. Flask V_1 (Fig. 2.XV) was evacuated, flamed-out and weighed before the anhydrous $H^{36}Cl$ was added. The flask was reweighed, attached to the vacuum line and the system pumped overnight. Initial background counts were obtained from both GM tubes. Tap I was closed and $H^{36}Cl$ admitted to the reaction vessel, which was then

isolated from the rest of the system by closing tap B. The amount of $H^{36}Cl$ in contact with the $FeCl_3$ was calculated as follows.

Pressure of $H^{36}Cl$ in line (measured by the manometer) = 228mm.

$\therefore$ number of mmol in reaction vessel = $\frac{PV}{RT}$

$$= \frac{0.30 \times 498.7}{82.053 \times 294}$$

$$= \underline{6.20 \text{ mmol}}.$$

After the addition of $H^{36}Cl$ (0.226g; 6.20 mmol) the count rate from both tubes was monitored for 5h. (Table 5.II). The $H^{36}Cl$ was removed by distillation into a trap held at 77K and a rose red colouration was observed. Background counts were obtained from both GM tubes and were essentially identical to those obtained initially. (Table 5.III)

BACKGROUND COUNTS

	G.M.1	G.M.2
Initial Counts Min^{-1}	208	146
Final Counts Min^{-1}	210	134

TABLE 5.III.

$H^{36}Cl$ AND REACTION VESSEL

Counts min^{-1} From G.M.1. +	-Background +	Corrected for Dead Time	Counts min^{-1} From G.M.2. +	-Background +	Corrected for Dead Time	(G.M.1-G.M.2) Counts min^{-1}	Time Min
1059	851	855	975	829	832	23	0
1034	826	829	943	797	800	29	2
1041	833	836	983	837	840	-4	4
1034	826	829	940	794	797	32	5
1139	931	935	1015	869	873	62	10
1077	869	873	1025	879	883	-10	15
1105	897	901	1025	879	883	18	20
1105	897	901	1079	933	937	-36	25
1142	934	938	1045	899	903	35	30
1049	841	844	1065	919	923	-79	35
1118	910	914	1124	978	983	-69	55
1117	909	913	1056	910	914	-1	90
1193	985	990	1159	1013	1018	-28	300

TABLE 5.II

The procedure described above was repeated using a second sample of $H^{36}Cl$. The results were identical except that the $H^{36}Cl$ removed after the experiment was complete was colourless at 77K.

5.1.2. Interaction of $FeCl_3$ and $H^{36}Cl$.

Iron(III) chloride [Sample A] (0.5120g; 3.16 mmol.) was weighed in a previously flamed-out reaction vessel in the inert atmosphere box. The flask containing the $FeCl_3$ was removed and evacuated before being attached to the counting vessel shown in Figure 2.XV. This system was pumped for several hours before the $FeCl_3$ was admitted to the movable boat and placed directly under one of the GM tubes. Background counts were obtained from both GM tubes. A known pressure (214 mm) of $H^{36}Cl$ (0.212g; 5.81 mmol in the reaction vessel) was admitted to the $FeCl_3$ and the system monitored for 3.5h. (Table 5.IV). The $H^{36}Cl$ was removed by distillation into a trap held at 77K. and background counts were obtained from both GM tubes. (Table 5.V).

Several reactions were performed using different ratios of $FeCl_3$ to anhydrous $H^{36}Cl$ and in each case similar results to those shown in Table 5.IV were obtained. Background counts obtained from both GM tubes after the reactions were essentially identical to those obtained initially. (Table 5.V).

$FeCl_3$ and $H^{36}Cl$

Counts min^{-1} in Solid & Gas Phases ↓	-Background ↓	Counts min^{-1} Corrected for Dead Time	Counts min^{-1} in Gas Phase ↓	-Background ↓	Counts min^{-1} Corrected for Dead Time ↓	Tubes Inter-calibrated	Surface Activity of $FeCl_3$ Counts min^{-1}	Time Min
1018	808	811	890	756	759	855	-44	0
1085	875	879	911	777	780	879	0	3
1092	882	886	924	790	793	894	-8	5
1036	826	829	863	729	732	825	4	15
1147	937	941	906	772	775	873	68	25
1145	935	939	939	805	808	910	29	35
1103	893	897	933	799	802	903	-6	45
1092	882	886	920	786	789	889	-3	55
1110	900	904	929	795	798	899	5	70
1117	907	911	970	836	840	947	-36	105
1180	970	975	989	855	859	968	7	120
1138	928	932	910	776	779	878	54	150
1143	933	937	955	821	824	929	8	180
1077	867	871	922	788	791	891	-20	210

TABLE 5.IV

BACKGROUND COUNTS FROM $FeCl_3$ and $H^{36}Cl$ REACTIONS.

	$FeCl_3$ mmol.	HCl mmol.	INITIAL BACKGROUND $FeCl_3$ Counts min^{-1}	INITIAL BACKGROUND Counts min^{-1}	FINAL BACKGROUND $FeCl_3$ Counts min^{-1}	FINAL BACKGROUND Counts min^{-1}
Sample A	3.16	5.81	159	142	151	148
Sample A	3.88	4.30	87	100	92	99
Sample A	0.94	1.90	190	210	201	195
Sample C	5.69	6.14	74	78	80	71

TABLE 5.V

When this reaction was repeated using $H^{36}Cl$ which was red when held at 77K, a different result was obtained. A known pressure (144mm) of $H^{36}Cl$ (0.142g; 3.89 mmol in the reaction vessel) was admitted to $FeCl_3$ (0.5120g; 3.16 mmol) and the system monitored for 1.5h (Table 5.VI). The $H^{36}Cl$ was removed by distillation and surface activity was detected on the $FeCl_3$. The surface activity of $FeCl_3$ decreased slightly on pumping overnight.

5.1.3. Interaction of $FeCl_3$ (Treated with water vapour) and $H^{36}Cl$.

Iron(III) chloride (0.6310g; 3.89 mmol) was placed under a G.M. tube as outlined in 5.1.2. A flask containing distilled water (Temp,= 298K; V.P. = 23.756mm Hg) was attached to the line at V_1 and the system pumped for

$FeCl_3$ + 'RED' $H^{36}Cl$

Counts min^{-1} in Solid & Gas Phases +	-Background +	Counts min^{-1} Corrected for Dead Time	Counts min^{-1} in Gas Phase +	-Background	Counts min^{-1} Corrected for Dead Time	Surface Activity of $FeCl_3$ Counts min^{-1}	Time Min
909	789	792	908	788	791	1	0
963	843	847	941	821	824	23	11
954	834	838	921	801	804	34	17
989	869	873	941	821	824	49	21
976	856	860	878	758	761	99	36
966	846	850	872	752	755	95	41
1035	915	919	920	800	803	116	51
1052	932	936	931	811	814	122	56
1022	902	906	874	754	757	149	61
1057	937	941	888	768	771	170	71
1073	953	958	913	793	796	162	76
1003	883	887	875	755	758	129	81
1066	946	950	899	779	782	168	86
1058	938	942	891	771	774	168	91

TABLE 5.VI

several hours. The flask was opened and the water vapour left in contact with the $FeCl_3$ for 3h. After this time, tap B was closed and the flask containing the distilled water removed. Flask V_1, which contained anhydrous $H^{36}Cl$, was attached to the line and the system pumped for several hours. A known pressure (288mm) of $H^{36}Cl$ (0.282g; 7.42 mmol in the reaction vessel) was admitted to the $FeCl_3$ and the system monitored for 3.8h. (Table 5.VII).

This reaction was repeated and the specific activity of each component assayed. A known pressure (198mm) of $H^{36}Cl$ (0.194g; 5.32 mmol) with a specific activity of 716 ± 31 counts $(5\ min)^{-1}\ mg^{-1}$ was admitted to $FeCl_3$ (0.1526g; 0.94 mmol.), which had been pretreated with water vapour, and the system monitored for 2h. (Table 5.VIII). The $H^{36}Cl$ was removed by distillation into a solution of NaOH, precipitated as $Ag^{36}Cl$ and its activity determined. (cf. 2.3.1) (Table 5.IX). The $FeCl_3$ was analysed by hydrolysing this sample, precipitating the iron as Fe_2O_3 and the $^{36}Cl^-$ as $Ag^{36}Cl$. (Table 5.X). The activity of the $FeCl_3$ was determined as AgCl. (Table 5.IX)

ANALYSIS OF $FeCl_3$.

	% Obtained	% Required for $FeCl_3$
Iron	34.1	34.4
Chlorine	63.8	65.6

TABLE 5.X.

$FeCl_3$ (TREATED WITH WATER VAPOUR) + $H^{36}Cl$. - I

	Counts min^{-1} In Solid & Gas Phases +	-Background +	Counts min^{-1} Corrected for Dead Time	Counts min^{-1} In Gas Phase +	-Background +	Counts min^{-1} Corrected for Dead Time	Surface Activity of $FeCl_3$ Counts min^{-1}	Time Min
	612	512	513	573	473	474	39	0
	561	461	462	531	431	432	30	2
	604	504	505	533	433	434	71	5
*	10131	8458	8480	8908	7241	7257	1223	7
	598	498	499	524	424	425	74	35
*	10209	8536	8560	8818	7151	7166	1394	37
	612	512	513	513	413	414	99	65
*	10097	8424	8445	8880	7213	7229	1216	67
	644	544	545	506	406	407	138	95
*	10201	8528	8550	8788	7121	7136	1414	97
	664	564	566	506	406	407	159	135
*	10150	8477	8499	8544	6877	6891	1608	147
*	10285	8562	8584	8679	7012	7027	1557	180
	661	561	562	499	399	400	162	220
*	10513	8840	8864	8582	6915	6929	1935	230

* Counted for 1000 secs.

TABLE 5.VII

$FeCl_3$ (Treated with Water Vapour) + $H^{36}Cl$ - II.

	Counts min^{-1} in Solid & Gas Phases →	-Background	Counts min^{-1} Corrected for Dead Time	Counts min^{-1} in Gas Phase →	-Background →	Counts min^{-1} Corrected for Dead Time →	Tubes Inter-calibrated	Surface Activity of $FeCl_3$. Counts min^{-1}	Time Min
	3294	2713	2750	2781	2544	2577	2749	1	0
*	12099	9194	9279	8983	7798	7859	8384	895	7
	2168	1587	1600	1592	1355	1364	1455	145	25
*	10944	8039	8104	7837	6652	6696	7143	961	37
	2229	1648	1662	1517	1280	1288	1374	288	50
*	11337	8432	8504	7709	6524	6567	7006	1498	67
	2346	1765	1781	1457	1220	1227	1309	472	75
*	11628	8723	8800	7621	6436	6478	6911	1889	97
	2390	1809	1826	1552	1315	1324	1412	414	100
	11739	8834	8913	7561	6376	6417	6846	2067	147

TABLE 5.VIII

SPECIFIC ACTIVITIES FROM $FeCl_3$ (TREATED WITH WATER VAPOUR) AND $H^{36}Cl$

Sample	Amount of $Ag^{36}Cl$ Counted mg.	(1)* Counts(5min)$^{-1}$ ±	(1) Counts(5min)$^{-1}$ mg^{-1} ±	(1) Counts(min)$^{-1}$ mg^{-1} Corrected for self absorption	(2) Amount of $Ag^{36}Cl$ Counted mg. ±	(2)* Counts(5min)$^{-1}$ ±	(2) Counts(5min)$^{-1}$ mg^{-1} ±	(2) Counts(5min)$^{-1}$ mg^{-1} Corrected for self absorption	Average Specific Activity Counts (5min)$^{-1}$mg^{-1}
Initial $H^{36}Cl$	17.0	11203	659	724	16.7	10838	649	708	716±31
Final $H^{36}Cl$	14.9	9580	643	639	15.7	9765	622	647	645±31
$FeCl_3$	22.0	860	39	52	22.4	918	41	55	54±3

* Counts corrected for dead time and background.

TABLE 5.IX

The radiochemical balance for this reaction is shown in the following calculation.

$$36.45g\ H^{36}Cl \equiv 143.32g\ Ag^{36}Cl.$$
$$0.194g\ H^{36}Cl \equiv 0.7628g\ Ag^{36}Cl.$$

$$162.2g\ FeCl_3 \equiv 3 \times 143.32g\ AgCl$$
$$\therefore 0.1526g\ FeCl_3 \equiv 0.4045g\ AgCl$$

The initial specific activity of $H^{36}Cl$, counted as $Ag^{36}Cl$ = 716 counts $(5min)^{-1}$ mg^{-1}

$\therefore$ the total initial activity of $H^{36}Cl$, counted as $Ag^{36}Cl = 0.7628 \times 10^3 \times 716 = 5.46 \times 10^5$ counts $(5min)^{-1}$

The total final activity of $H^{36}Cl$, counted as $Ag^{36}Cl$

$$= 0.7628 \times 10^3 \times 645$$
$$= \underline{4.92 \times 10^5 \text{ counts } (5min)^{-1}}$$

The total final activity of $FeCl_3$ counted as $Ag^{36}Cl$

$$= 0.4045 \times 10^3 \times 54$$
$$= \underline{2.18 \times 10^4 \text{ counts } (5min)^{-1}}$$

$\therefore$ The total final activity = 5.14×10^5 counts $(5min)^{-1}$ which is in good agreement with the initial amount of activity.

5.1.4. Interaction of '$FeCl_3.H_2O$' and $H^{36}Cl$.

A solid whose overall composition corresponded to $FeCl_3.H_2O$ was prepared by mixing $FeCl_3$ (1.0969g; 6.76mmol) with distilled water (0.1217g; 6.76 mmol). $FeCl_3$ was weighed in the inert atmosphere box, removed and placed in a small beaker. The water was syringed

on to the $FeCl_3$ and the resulting sticky compound was placed in the movable boat. The boat was returned to the reaction vessel and the system pumped for several hours before $H^{36}Cl$ (0.2664g; 7.31 mmol) was admitted to the '$FeCl_3.H_2O$'. (0.360g; 1.99 mmol). The count rate from both tubes was monitored for 3.5h. (Table 5.XI). The $H^{36}Cl$ was removed by distillation and the count rate from each tube monitored.

5.1.5. Interaction of $FeCl_3.6H_2O$ and $H^{36}Cl$.

Iron(III) chloride hexahydrate (0.6717g; 2.49 mmol) was placed under a GM tube as outlined in 5.1.2. A known pressure (214 mm) of $H^{36}Cl$ (0.210g; 5.76 mmol in the reaction vessel) was admitted to the reaction vessel and the system monitored for 2.75h. (Table 5.XII). The $H^{36}Cl$ was removed by distillation and the count rate from both tubes monitored.

This reaction was repeated and the specific activity of each component assayed. A known pressure (479mm) of $H^{36}Cl$ (0.4702g; 12.9 mmol) with a specific activity of 901 ± 32 counts $(5\ min)^{-1}\ mg^{-1}$ was admitted to $FeCl_3.6H_2O$ (1.5615g; 5.78 mmol) and the system monitored for 3.3h. (Table 5.XIII). The $H^{36}Cl$ was removed by distillation into a solution of NaOH, precipitated as $Ag^{36}Cl$ and its activity determined. (Table 5.XIV). The $FeCl_3.6H_2O$ was analysed by hydrolysing the sample and precipitating the iron as Fe_2O_3 and the $^{36}Cl^-$ as $Ag^{36}Cl$. (Table 5.XV). The specific activity of the $FeCl_3.6H_2O$ was determined as $Ag^{36}Cl$. (Table 5.XIV).

'$FeCl_3.H_2O$' AND $H^{36}Cl$.

	Counts min^{-1} in Solid & Gas Phases +	Background +	Counts min^{-1} Corrected for Dead Time	Counts Min^{-1} in Gas Phase +	Background +	Counts min^{-1} Corrected for Dead Time +	Tubes Inter-calibrated	Surface Activity of $FeCl_3$. Counts min^{-1}	Time Min
	677	602	604	723	657	659	706	-102	0
	797	722	725	567	501	502	538	187	5
*	15195	13945	14004	9200	8100	8120	8700	5304	7
	942	867	871	558	492	493	528	343	25
	965	890	894	519	453	454	486	408	30
*	16697	15447	15519	8489	7389	7405	7934	7585	37
	1047	972	977	495	429	430	461	516	55
*	17187	15937	16014	8155	7055	7070	7575	8439	67
	1066	991	996	497	431	432	463	533	90
*	17629	16379	16460	8177	7077	7092	7599	8861	97
	1071	996	1001	476	410	411	440	561	115
*	18566	17316	17406	7942	6842	6856	7346	10060	147
	1144	1069	1075	434	418	419	449	626	195
*	18464	17214	17303	7642	6542	6555	7023	10280	197

* Counted for 1000 secs.

TABLE 5XI

$FeCl_3.6H_2O$ AND $H^{36}Cl$. - RUN I.

	Counts min^{-1} in Solid & Gas Phases →	-Background →	Counts min^{-1} Corrected for Dead Time →	Tubes Inter-Calibrated	Counts min^{-1} in Gas Phase →	-Background →	Counts min^{-1} Corrected for Dead Time	Surface Activity of $FeCl_3$. Counts min^{-1}	Time Min
	589	504	505	523	466	378	379	144	0
	851	766	769	796	336	268	268	528	5
*	16832	15415	15487	16034	5310	3843	3847	12187	7
	1045	957	962	996	277	189	189	807	25
	1162	1077	1083	1121	261	173	173	948	35
*	17657	16240	16320	16896	4312	2845	2847	14049	37
	1106	1021	1026	1062	269	181	181	881	55
	1078	993	998	1033	243	155	155	878	65
*	17622	16205	16284	16859	4045	2578	2580	14279	67
	1100	1015	1020	1056	216	128	128	928	95
*	17257	15840	15916	16478	3870	2403	2406	14072	97
	998	913	917	949	194	106	106	843	140
*	16811	15394	15465	16011	3683	2216	2217	13794	147
	994	909	913	945	213	125	125	820	165

* Counted for 1000 secs.

TABLE 5.XII

$FeCl_3.6H_2O$ AND $H^{36}Cl$ - RUN II

Counts min^{-1} in Solid & Gas Phases ±	Background ±	Counts min^{-1} Corrected for Dead Time	Counts min^{-1} in Gas Phase ±	Background ±	Counts min^{-1} Corrected for Dead Time	Surface Activity of $FeCl_3$. Counts min^{-1}	Time Min
17403	17208	18828	11534	11334	12015	6813	0
21480	21285	23820	9787	9587	10070	13750	5
21975	21780	24442	7820	7620	7922	16520	7
21935	21740	24391	6018	5818	5992	18399	25
21701	21506	24097	5395	5195	5334	18763	35
21545	21350	23902	5090	4890	5012	18890	37
21102	20907	23348	4512	4312	4407	18941	55
21113	20918	23361	4310	4110	4196	19165	65
20684	20489	22828	4338	4138	4225	18603	67
20411	20216	22489	3824	3624	3691	18798	95
20215	20020	22247	3773	3573	3637	18610	97
20102	19907	22108	3648	3448	3508	18600	140
19988	19793	21967	3418	3218	3271	18686	147
20305	20110	22358	3396	3196	3248	19110	165

TABLE 5.XIII

SPECIFIC ACTIVITIES FROM $FeCl_3.6H_2O + H^{36}Cl$

Sample	(1) Amount of $Ag^{36}Cl$ Counted mg.	(1) * Counts(5min)$^{-1}$ ±	(1) Counts(5min)$^{-1}$mg^{-1} ±	(1) Counts(min)$^{-1}$mg^{-1} Corrected for self absorption	(2) Amount of $Ag^{36}Cl$ Counted mg. ±	(2)* Counts(5min)$^{-1}$ ±	(2) Counts(5min)$^{-1}$mg^{-1} ±	Counts(5min)$^{-1}$mg^{-1} Corrected for self absorption	Average Specific Activity Counts(5min)$^{-1}$mg^{-1}
Initial $H^{36}Cl$	23.7	14599	616	892	18.8	14532	773	910	901±32
Final $H^{36}Cl$	24.6	6674	271	392	23.2	6412	276	380	386±13
$FeCl_3$	25.1	6530	260	383	22.9	5911	258	351	367±13

* Counts corrected for dead time and background.

TABLE 5.XIV

ANALYSIS OF $FeCl_3.6H_2O$.

	% Obtained	% Required for $FeCl_3.6H_2O$
Iron	20.0	20.7
Chlorine	38.8	39.4

TABLE 5.XV

The radiochemical balance for this reaction is shown in the following calculation.

36.45g HCl ≡ 143.32g AgCl

∴ 0.4702g HCl ≡ 1.85g AgCl.

270.2g $FeCl_3.6H_2O$ ≡ 3 x 143.32g AgCl

∴ 1.5615g $FeCl_3.6H_2O$ ≡ 2.49g AgCl.

The initial specific activity of $H^{36}Cl$, counted as $Ag^{36}Cl$ = 901 counts $(5min)^{-1}$ mg^{-1}

∴ the total initial activity of $H^{36}Cl$, counted as $Ag^{36}Cl$

$= 1.85 \times 10^3 \times 901$

$= \underline{1.67 \times 10^6 \text{ counts } (5min)^{-1}}$

The total final activity of $H^{36}Cl$, counted as $Ag^{36}Cl$

$= 1.85 \times 10^3 \times 386$

$= \underline{7.14 \times 10^5 \text{ counts } (5min)^{-1}}$

The total final activity of $FeCl_3.6H_2O$, counted as $Ag^{36}Cl$

$= 2.49 \times 10^3 \times 367$

$= \underline{9.14 \times 10^5 \text{ counts } (5min)^{-1}}$

. . The total final activity = 1.63×10^6 counts $(5min)^{-1}$ which is in good agreement with the initial value.

5.1.6. Interaction of $[(C_2H_5)_4N][FeCl_4]$ and $H^{36}Cl$.

Tetraethylammonium tetrachloroferrate (0.4427g; 1.35 mmol) was placed under a GM tube as outlined in 5.1.2. $H^{36}Cl$ (0.2435g; 6.68 mmol) was admitted to the reaction vessel and the system monitored over a period of 2h. (Table 5.XVI). The $H^{36}Cl$ was removed and the background reading taken. (Table 5.XVII).

BACKGROUND READINGS

	G.M.1 $[(C_2H_5)_4N][FeCl_4]$	G.M.2
Initial Counts min^{-1}	74	75
Final Counts min^{-1}	79	75

TABLE 5.XVII

5.2. RESULTS

5.2.1. Interaction of $H^{36}Cl$ with the glass reaction vessel.

When $H^{36}Cl$ (0.226g; 6.20 mmol) is admitted to the reaction vessel at room temperature, the count rates from both GM tubes are identical and remain constant over a period of 5h. The initial and final background

$[(C_2H_5)_4N][FeCl_4]$ AND $H^{36}Cl$

	Counts min^{-1} in Solid & gas Phases →	-Background →	Counts min^{-1} Corrected for Dead Time →	Tubes Intercalibrated	Counts min^{-1} in Gas Phase →	-Background →	Counts min^{-1} Corrected for Dead Time	Surface Activity of $FeCl_3$ Counts min^{-1}	Time Min.
	500	434	435	486	561	486	487	-1	0
	528	462	463	517	605	530	531	-14	5
*	8840	7740	7758	8379	9555	8305	8326	53	7
	497	431	432	482	594	519	520	-38	25
	534	468	469	524	591	516	517	7	35
*	8742	7642	7660	8273	9559	8309	8330	-57	37
	544	478	479	535	575	500	501	34	60
	530	464	465	519	557	482	483	36	65
*	8764	7664	7682	8297	9498	8248	8268	29	67
	498	432	433	483	587	512	513	-30	85
	552	486	487	543	571	496	497	46	95
*	8924	7824	7842	8469	9533	8283	8304	165	97
	526	460	461	514	595	520	521	-7	120
*	8699	7599	7616	8225	9499	8249	8270	-45	122

* Counted for 1000 secs.

TABLE 5.XVI

readings are identical, within the uncertainty in the count, and indicate that $H^{36}Cl$ is not adsorbed by the reaction vessel. Similar behaviour is exhibited when this reaction is repeated with fresh $H^{36}Cl$.

5.2.2. Interaction of $FeCl_3$ and HCl.

When $H^{36}Cl$ (0.212g; 5.81 mmol) is admitted to $FeCl_3$ (0.512g; 3.16 mmol) the count rate from the gas plus solid and that from the gas alone remain constant. On removal of $H^{36}Cl$, the background reading obtained from each tube is identical to the value obtained for the initial reading. This shows that neither exchange nor adsorption occurs between anhydrous $H^{36}Cl$ and anhydrous $FeCl_3$ at room temperature. This reaction was repeated with different samples of $FeCl_3$ and $H^{36}Cl$ and the same results obtained.

This reaction was carried out using $H^{36}Cl$ which was red when held at 77K and when this $H^{36}Cl$ (0.142g; 3.89 mmol) is admitted to anhydrous $FeCl_3$ (0.5120g; 3.16 mmol), the count rate from the gas plus solid increases with time and that from the gas alone decreases. The difference in count rate gives the surface ^{36}Cl activity of $FeCl_3$, and the variation of this with time is shown in Figure 5.I. The surface activity is retained when $H^{36}Cl$ is removed though it decreases slightly after overnight pumping.

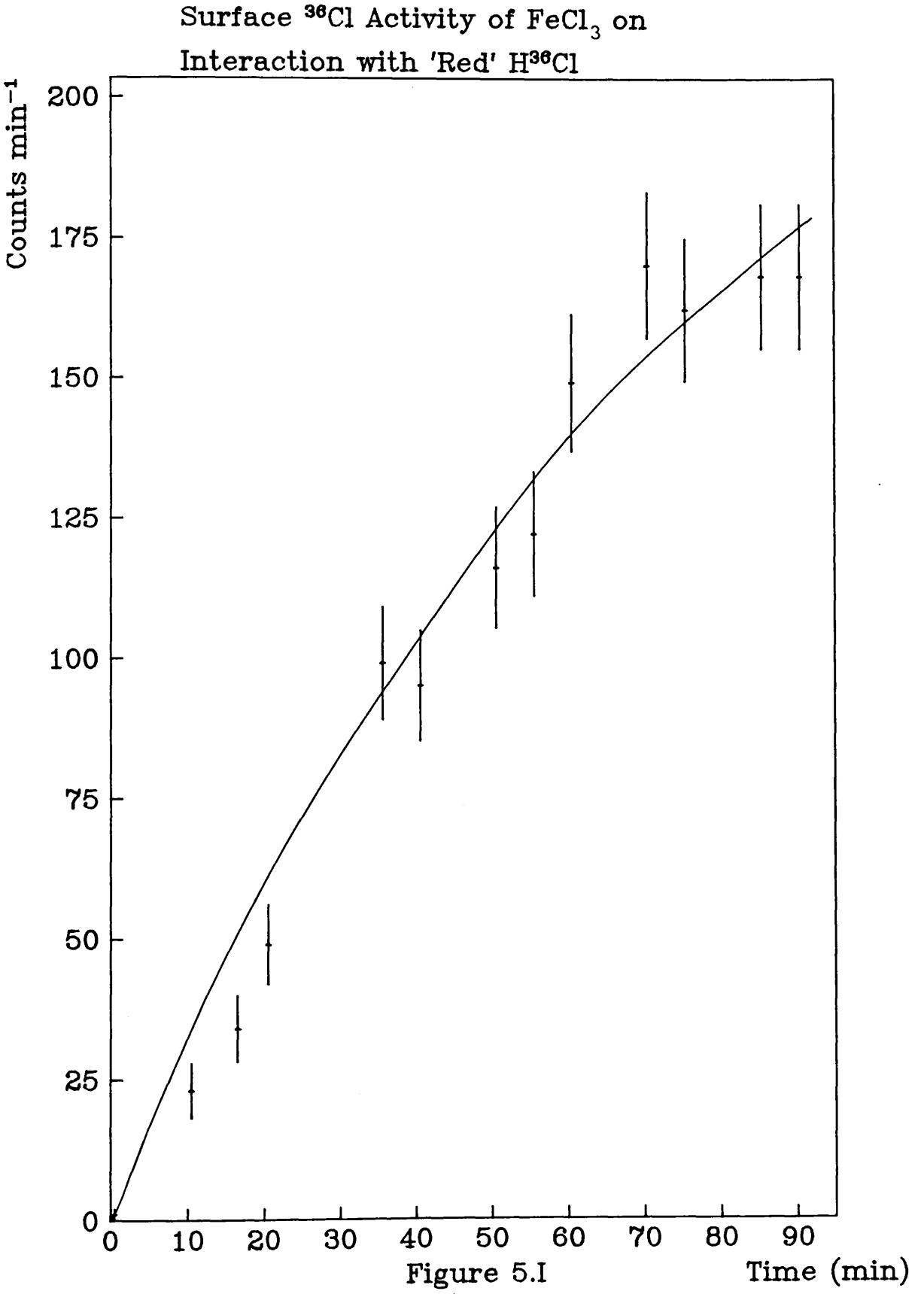

Surface ^{36}Cl Activity of $FeCl_3$ on
Interaction with 'Red' $H^{36}Cl$
Counts min^{-1}
200
175
150
125
100
75
50
25
0
0
10
20
30
40
50
60
70
80
90
Time (min)

Figure 5.I

5.2.3. Interaction of $FeCl_3$ (Treated with water vapour) and $H^{36}Cl$.

When $H^{36}Cl$ (0.282g; 7.74 mmol) is admitted to $FeCl_3$ (0.6310g; 3.89 mmol), which has been previously treated with water vapour, the count rate from the gas plus solid increases with time and that from the gas alone decreases. The variation of the surface ^{36}Cl activity of $FeCl_3$ with time is shown in Figure 5.II. The surface activity is unaffected by the removal of $H^{36}Cl$ from the gas phase though it decreases slightly after overnight pumping. The apparent fraction of ^{36}Cl activity exchanged between $H^{36}Cl$ and $FeCl_3$(f) is ca 30% after 2h. (Table 5.XVIII).

Repetition of this reaction using $FeCl_3$ (0.1526g; 0.94 mmol), which has been previously treated with water vapour, and $H^{36}Cl$ (0.194g; 5.32 mmol) gave rise to similar results though the apparent fraction of ^{36}Cl activity (f), is greater. (Table 5.XVIII). Analysis of $FeCl_3$, after $H^{36}Cl$ has been removed, indicates that the ratio Fe:Cl is 1:3.0 and that $FeCl_3$ is slightly active. (Table 5.XIX). Analysis of the $H^{36}Cl$, before and after the reaction, shows that the specific activity of the $H^{36}Cl$ has decreased.

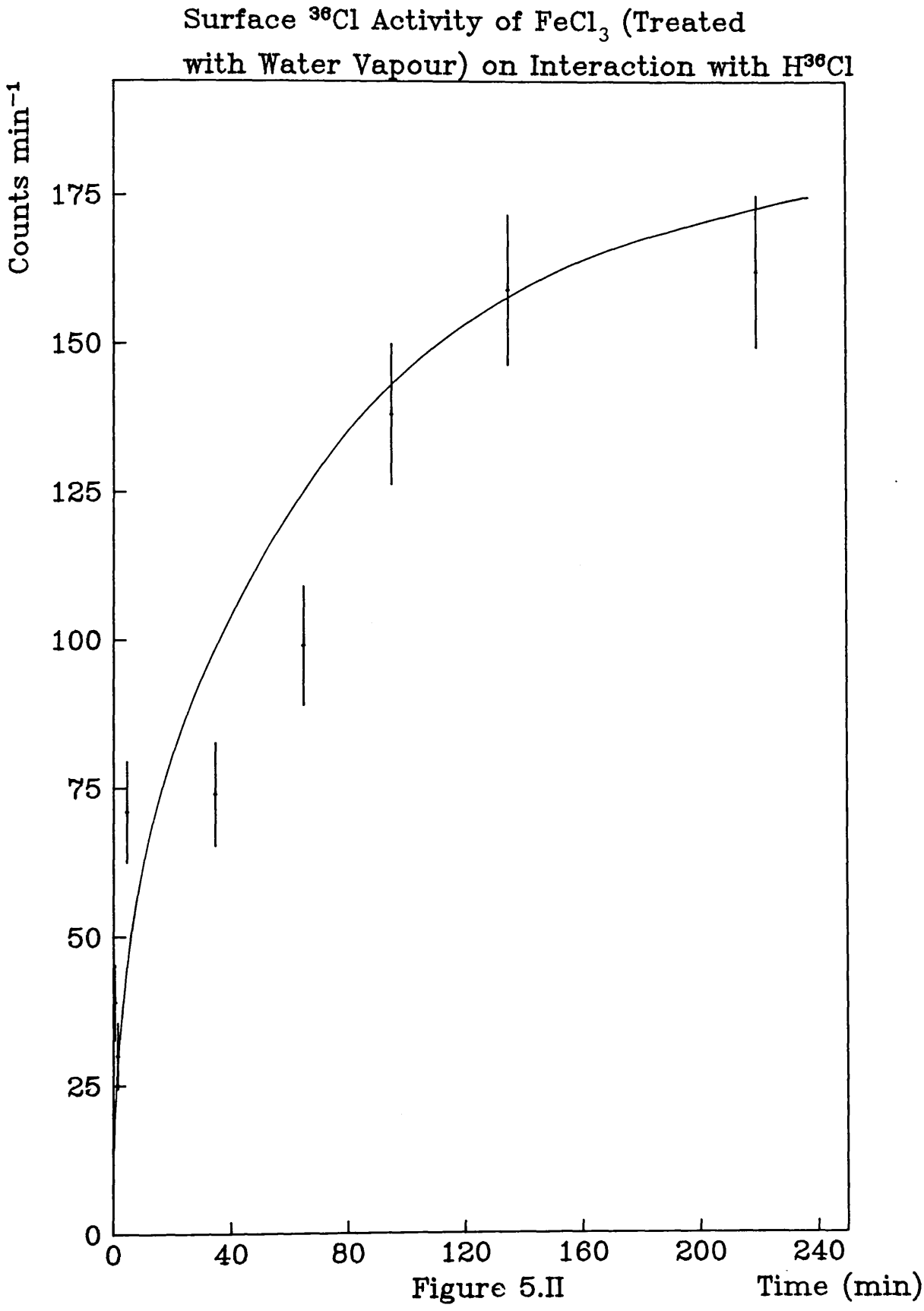

Surface ^{36}Cl Activity of $FeCl_3$ (Treated with Water Vapour) on Interaction with $H^{36}Cl$
Counts min^{-1}
175
150
125
100
75
50
25
0
0
40
80
120
160
200
240
Time (min)

Figure 5.II

Apparent Fraction of ^{36}Cl Activity Exchanged.

Time (Min)	7	37	67	97	147
f-value for $FeCl_3$ (Treated with water vapour)-I	0.24 ± 0.01	0.27 ± 0.01	0.24 ± 0.01	0.28 ± 0.01	0.32 ± 0.01
f-value for $FeCl_3$ (Treated with water vapour)-II	0.28 ± 0.01	0.34 ± 0.01	0.51 ± 0.02	0.62 ± 0.02	0.67 ± 0.02
f-value for $FeCl_3.H_2O$	0.84 ± 0.02	1.09 ± 0.02	1.17 ± 0.03	1.20 ± 0.03	1.29 ± 0.03
f-value for $FeCl_3.6H_2O$.I	1.35 ± 0.03	1.47 ± 0.03	1.50 ± 0.03	1.51 ± 0.03	1.53 ± 0.03
f-value for $FeCl_3.6H_2O$.II	1.18 ± 0.03	1.38 ± 0.03	1.42 ± 0.03	1.46 ± 0.03	1.48 ± 0.03

TABLE 5.XVIII.

SPECIFIC ACTIVITIES FROM THE INTERACTION OF $FeCl_3$ (TREATED WITH WATER VAPOUR) AND $H^{36}Cl$.

Sample	Specific Activity Counts $(5min)^{-1}$ mg^{-1}
Initial $H^{36}Cl$, counted as $Ag^{36}Cl$	716 ± 31
Final $H^{36}Cl$, counted as $Ag^{36}Cl$	645 ± 31
$Fe^{36}Cl_3$, counted as $Ag^{36}Cl$	54 ± 3

TABLE 5.XIX

Complete exchange between $H^{36}Cl$ and $FeCl_3$ would result in ^{36}Cl specific activities of 468 ± 20 counts $(5min)^{-1}$ mg^{-1}. The value obtained for $H^{36}Cl$ is higher than this and that for $FeCl_3$ very much lower, indicating that only partial exchange has occurred. The fraction of ^{36}Cl activity exchanged, calculated from the specific activity measurements, is 0.12 ± 0.02. The difference in the f-values, calculated from the total counts and surface activities and those calculated from the specific activity measurements, gave an indication of the quantity of $H^{36}Cl$ retained by the $FeCl_3$. In this case, $H^{36}Cl$ is adsorbed by the $FeCl_3$. The amount of $H^{36}Cl$ adsorbed is

estimated in the following calculation.

The difference in the f-values is 0.55.

Assuming that the total count from the gas plus solid phase will be the same then the number of counts, x, from the solid phase due to adsorbed $H^{36}Cl$ is calculated from

$$\frac{\frac{x}{8913}}{\frac{3 \times \text{mmol } FeCl_3}{3 \times \text{mmol } FeCl_3 + 1 \text{ mmol } H^{36}Cl}} = 0.55.$$

$$\Rightarrow \quad \frac{\frac{x}{8913}}{0.3464} = 0.55$$

$$\therefore \quad x = 0.55 \times 0.3464 \times 8913$$

$$= \underline{1698 \text{ counts min}^{-1}}$$

From the graph showing the pressure of $H^{36}Cl$ vs counts, this is equivalent to a pressure of 66 mm.

$$\text{The number of mmol. of } H^{36}Cl \text{ present} = \frac{0.087 \times 498.7}{82.053 \times 296}$$

$$= \underline{1.78 \text{ mmol}}.$$

$$\therefore \text{ The number of } H^{36}Cl \text{ molecules adsorbed}$$

$$= 1.78 \times 10^{-3} \times 6.022 \times 10^{23}$$

$$= \underline{1.07 \times 10^{21}}$$

5.2.4. Interaction of '$FeCl_3.H_2O$' and $H^{36}Cl$.

When $H^{36}Cl$ (0.2664g; 7.31 mmol) is admitted to a solid, whose overall composition corresponds to $FeCl_3.H_2O$, (0.360g; 1.99 mmol) the count rate from the gas plus solid increases with time and that from the gas alone decreases. The difference in count rates gives the surface ^{36}Cl activity of $FeCl_3$, and the variation of this with time is shown in Figure 5.III. The surface activity is unaffected by the removal of $H^{36}Cl$ from the gas phase though it decreases from 10280 counts min^{-1} to 8834 counts min^{-1}, after overnight pumping. The apparent fraction of ^{36}Cl activity exchanged between $H^{36}Cl$ and '$FeCl_3.H_2O$', (f), has been calculated at various stages of the reaction. (Table 5.XVIII). In this reaction, the f-value is greater than 1, after only 37 min.

5.2.5. Interaction of $FeCl_3.6H_2O$ and $H^{36}Cl$.

When $H^{36}Cl$ (0.2101g; 5.76 mmol) is admitted to $FeCl_3.6H_2O$ (0.6717g; 2.49 mmol) the count rate from the gas plus solid increases with time and that from the gas alone decreases. The variation of the surface ^{36}Cl activity of $FeCl_3$ with time is shown in Figure 5.IV. The surface activity is unaffected by the removal of $H^{36}Cl$ from the gas phase though it decreases after overnight pumping. The apparent fraction of ^{36}Cl activity exchanged between $H^{36}Cl$ and $FeCl_3.6H_2O$, f, has been calculated at various stages of the reaction. (Table 5.XVIII). After only 7 min, the f-value is

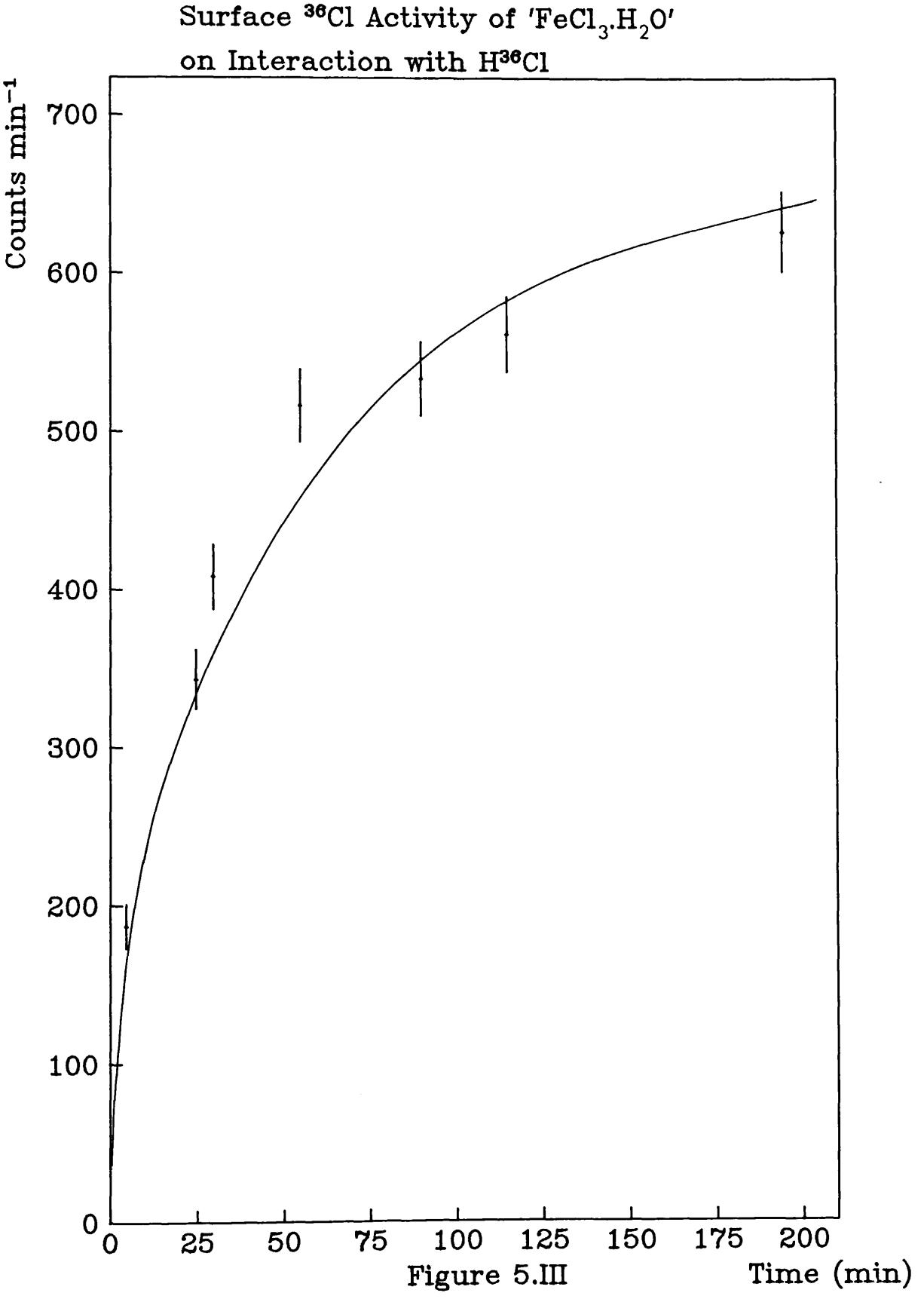

Surface ^{36}Cl Activity of '$FeCl_3.H_2O$'
on Interaction with $H^{36}Cl$
Counts min^{-1}
700
600
500
400
300
200
100
0
0
25
50
75
100
125
150
175
200
Time (min)

Figure 5.III

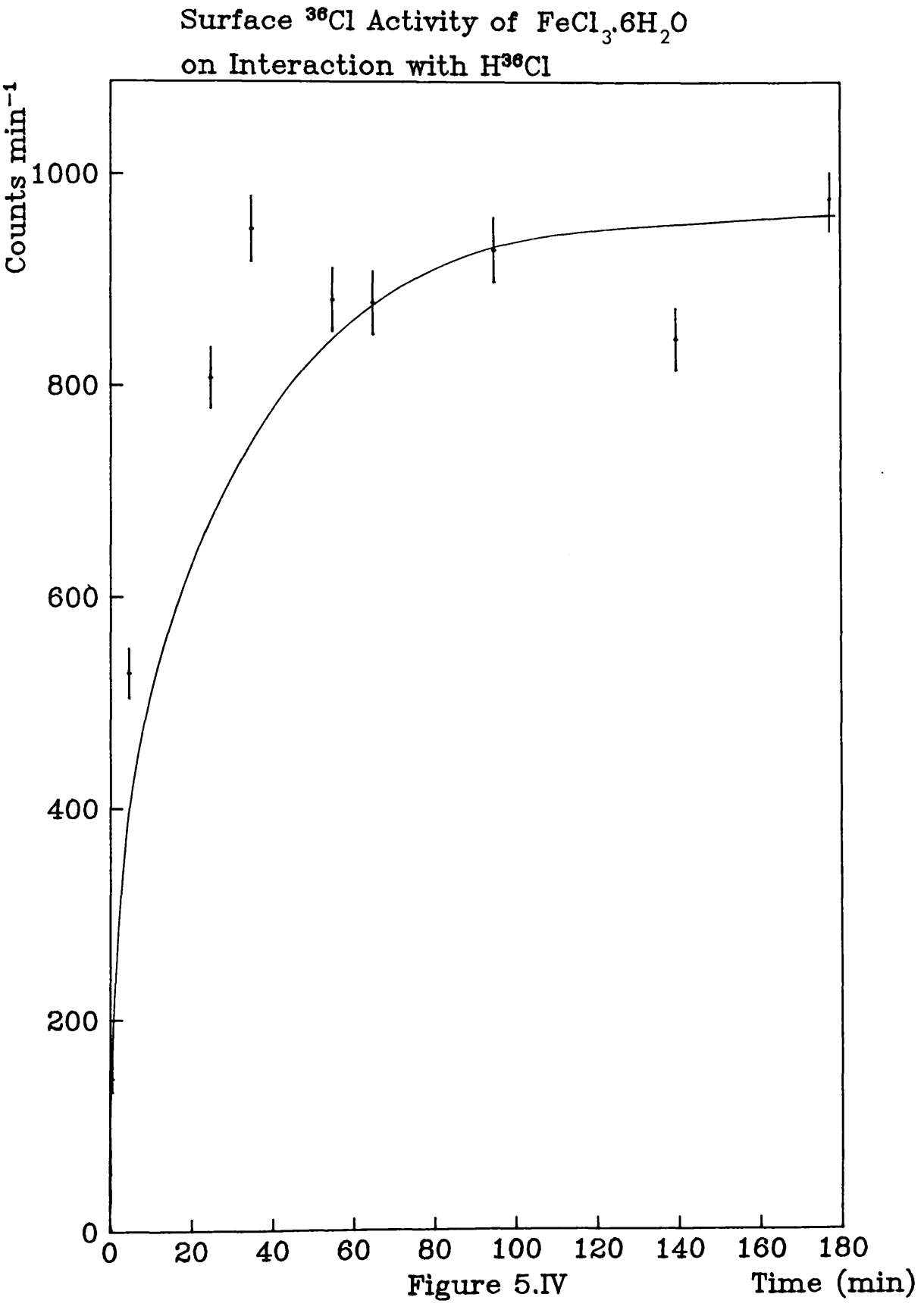

Surface ^{36}Cl Activity of $FeCl_3.6H_2O$
on Interaction with $H^{36}Cl$
Counts min^{-1}
1000
800
600
400
200
0
0
20
40
60
80
100
120
140
160
180
Time (min)

Figure 5.IV

greater than 1.

This reaction was repeated using $FeCl_3.6H_2O$ (1.5616g; 5.78 mmol) and $H^{36}Cl$ (0.4702g; 12.9 mmol) with similar results. (table 5.XVIII). Analysis of $FeCl_3.6H_2O$, after $H^{36}Cl$ has been removed, indicates that the ratio Fe:Cl is 1:3.0 and that $FeCl_3.6H_2O$ is active. (Table 5.XX). Analysis of the $H^{36}Cl$, before and after the reaction, shows that the specific activity of the $H^{36}Cl$ has decreased. Complete exchange between $H^{36}Cl$ and $FeCl_3$ would result in ^{36}Cl specific activities of 384 ± 14 counts $(5\ min)^{-1}\ mg^{-1}$. This value is identical, within the error limits,

SPECIFIC ACTIVITIES FROM THE INTERACTION OF $FeCl_3.6H_2O$ AND $H^{36}Cl$.

Sample	Specific Activity Counts $(5min)^{-1}mg^{-1}$
Initial $H^{36}Cl$, counted as $Ag^{36}Cl$	901 ± 32
Final $H^{36}Cl$, counted as $Ag^{36}Cl$	386 ± 13
$Fe^{36}Cl_3$, counted as $Ag^{36}Cl$	367 ± 13

TABLE 5.XX

to the values obtained for the specific activities. The fraction of ^{36}Cl activity exchange has also been calculated

from the specific activity measurements and found to be 1.00 ± 0.02. The difference in the f-values, calculated from the total counts and surface activities and those calculated from the specific activity indicate the $H^{36}Cl$ is being retained by the surface. The amount of $H^{36}Cl$ adsorbed is estimated in the following calculation.

The difference in the f-values = 0.48

Therefore, the number of counts (x) from the gas phase due to adsorbed $H^{36}Cl$ is calculated from

$$\frac{\frac{x}{21967}}{0.5734} = 0.48$$

$$\therefore x = 0.48 \times 0.5734 \times 21967$$

$$= \underline{6046 \text{ counts min}^{-1}}$$

This is equivalent to a pressure of 287 mm.

The number of mmol. of $H^{36}Cl$ present $= \frac{0.378 \times 498.7}{82.053 \times 297}$

$$= \underline{\underline{7.73 \times \quad \text{mmol}}}.$$

$\therefore$ The number of $H^{36}Cl$ molecules adsorbed

$$= 7.73 \times 10^{-3} \times 6.022 \times 10^{23}$$

$$= \underline{\underline{4.65 \times 10^{21}}}$$

5.2.6. Interaction of $[(C_2H_5)_4N][FeCl_4]$ and $H^{36}Cl$.

When $H^{36}Cl$ (0.2435g; 6.68 mmol) is admitted to $[(C_2H_5)_4N][FeCl_4]$ (0.4427g; 1.35 mmol), the count rate from the gas plus solid and that from the gas alone

remain constant. The initial and final background readings are identical. This indicates that neither exchange nor adsorption occur.

5.3. DISCUSSION.

A sample of $H^{36}Cl$ was purified as outlined in 2.4.1. and was colourless at 77K. After prolonged exposure to the vacuum line this sample gave a rose-red colour when held at 77K. This red form of solid HCl at 77K has been previously observed[88] and it was noted that the red colour disappears when the solid is warmed to 98K, which is the transition temperature between two crystalline modifications of HCl.[58] Mass spectrographic analysis showed less than 0.1% of any impurity in the mass range 6 to 100. The addition of small quantities of H_2, O_2, N_2, Cl_2, Hg and NO_2 had no effect on the production of the red colour whilst the addition of 10^{-4} - 10^{-5} mole fraction of NO intensified the red colour. It has been suggested, from this evidence, that the red colour is not due to separable impurities in HCl but is caused by imperfections in its crystal lattice and that traces of NO favours the production of these imperfections.[89] It was shown, however, when HCl was slowly vacuum distilled from 133K to 77K that it failed to produce a red colour. This suggests that the red form of solid HCl at 77K is due to separable impurity. The impurity is probably not red at 77K but produces crystal imperfections in solid HCl.[58] The final step in the purification process of the $H^{36}Cl$ used in these reactions

involves vacuum distillation from 133K to 77K but prolonged exposure of the $H^{36}Cl$ to the vacuum system results in the reappearance of the red colour at 77K. When this $H^{36}Cl$ is reacted with $FeCl_3$, the count rate from the gas plus solid increases with time and that from the gas alone decreases which suggests that either ^{36}Cl exchange between $H^{36}Cl$ and $FeCl_3$ or adsorption of $H^{36}Cl$ by $FeCl_3$ occurs. It is possible that $H^{36}Cl$ becomes contaminated by trace amounts of water from the surface of the glass apparatus and that water causes crystal imperfections in the solid HCl which results in the red colour at 77K.

Hydrogen chloride does not exchange with iron(III) chloride under anhydrous conditions nor is it adsorbed by the surface. When this reaction is repeated using $FeCl_3$, which has previously been treated with water vapour, exchange occurs to some extent. Presumably water reacts with $FeCl_3$ to give $[Fe(H_2O)_4Cl_2]^+[FeCl_4]^-$ (cf. Table 5.I) and, assuming that this reaction occurs on the surface, the chemical identity of the catalyst has now changed. ^{36}Cl exchange must result from the interaction of $H^{36}Cl$ with either $[Fe(H_2O)_4Cl_2]^+$ or $FeCl_4^-$. No exchange, however, occurs between $FeCl_4^-$, as its tetraethylammonium salt, and $H^{36}Cl$. This is surprising since tetrahedral $FeCl_4^-$, which is a high-spin d^5 complex, is expected to be labile. This suggests that although the equilibrium

$$FeCl_3 + HCl \rightleftharpoons H^+FeCl_4^-$$

exists in solution it does not occur at room temperature between anhydrous $FeCl_3$ and anhydrous HCl. This could be because either H^+ needs to be solvated or molecular $FeCl_3$ is not involved. It must be the interaction between $[Fe(H_2O)_4Cl_2]^+$ and $H^{36}Cl$ which results in ^{36}Cl exchange and this could occur either as shown in diagram 5.I or by coordinatively unsaturated Fe^{III} cations on the surface providing active sites.

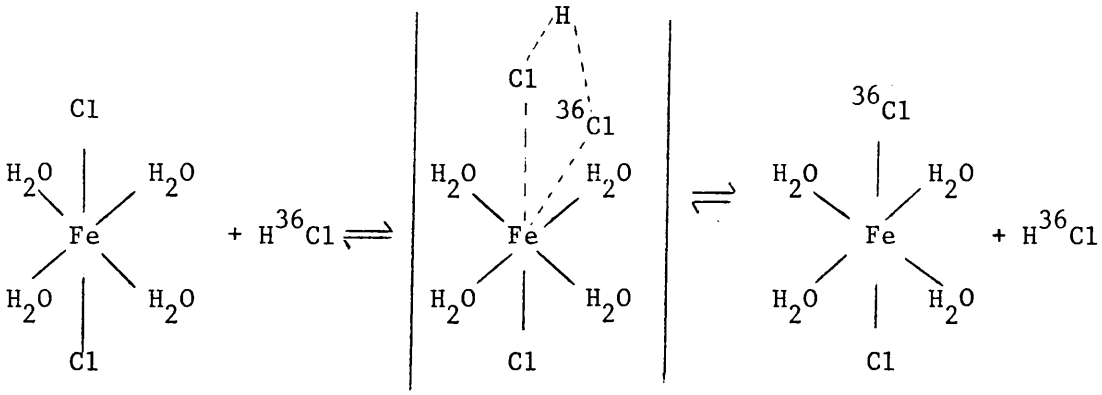


DIAGRAM 5.I

The difference in the f-values, calculated from the total counts and surface activities and those calculated from the specific activity measurements, indicate that $H^{36}Cl$ is adsorbed by the $FeCl_3$ surface. Analysis of the $FeCl_3$ shows that the correct ratio Fe:Cl of 1:3.0 is obtained which suggests that any adsorbed $H^{36}Cl$ is lost in the work-up procedure during analysis.

It has been suggested, when $FeCl_3$ is used as a catalyst in the preparation of some chlorohydrocarbons (cf. 1.4.1.), that the catalytically active species is $FeCl_3.H_2O$. Although there is no evidence for the

existence of this compound, exchange reactions were performed between $H^{36}Cl$ and a sticky compound whose overall composition corresponds to $FeCl_3.H_2O$. This compound is probably a mixture of the known hydrates and will have the structure $[FeCl_2(H_2O)_4]^+[FeCl_4]^- xH_2O$. When $H^{36}Cl$ is admitted to '$FeCl_3.H_2O$' the count rate from the gas plus solid increases with time and that from the gas alone decreases. The apparent fraction of ^{36}Cl activity exchange between $H^{36}Cl$ and '$FeCl_3.H_2O$' is greater than 1 after 37 min. This evidence suggests that ^{36}Cl exchange occurs between $H^{36}Cl$ and '$FeCl_3.H_2O$', in an analogous manner to that observed between $H^{36}Cl$ and $FeCl_3$ (treated with water vapour), and that $H^{36}Cl$ is adsorbed by the surface, since the apparent fraction of ^{36}Cl activity has values greater than 1.

Complete ^{36}Cl exchange occurs between $H^{36}Cl$ and $FeCl_3.6H_2O$, which exists as $[Fe(H_2O)_4Cl_2]^+ Cl^-.2H_2O$, and this could occur via a reaction between the chloride ion and $H^{36}Cl$ (Diagram 5.II) followed

$$Cl^- + H^{36}Cl \rightleftharpoons [Cl^- \text{-----} H \text{-----} {}^{36}Cl] \rightleftharpoons HCl + {}^{36}Cl^-$$

Diagram 5.II

by either exchange of $^{36}Cl^-$ with $H^{36}Cl$ or with Fe-Cl as depicted in diagram 5.I. The difference in the f-values, calculated from the total counts and surface activities and those calculated from the specific activity measurements, indicate that $H^{36}Cl$ is adsorbed by the $FeCl_3.6H_2O$. Analysis of $FeCl_3.6H_2O$ shows

that the correct ratio Fe;Cl of 1:3·0 is obtained which suggests that any adsorbed $H^{36}Cl$ is lost in the work-up procedure during analysis.

The comparison between the increase in surface ^{36}Cl activity for $FeCl_3$ (pretreated with water vapour) and $H^{36}Cl$, '$FeCl_3.H_2O$' and $H^{36}Cl$ and $FeCl_3.6H_2O$ and $H^{36}Cl$ is shown in Figure 5.V. Water, obviously has a strong labilising effect towards the Fe(III)-Cl bond in the reaction between $FeCl_3$ and $H^{36}Cl$.

Vinylidene chloride reacts with HCl in the presence of iron(III) chloride to give 1,1,1,trichloroethane (cf. 1.4.3) and it has been suggested that anhydrous $FeCl_3$ causes ionization of HCl followed by protonation of vinylidene chloride with subsequent addition of a chloride ion to give 1,1,1-trichloroethane (scheme 5.I)

$$FeCl_3 + HCl \rightleftharpoons H^+FeCl_4^-$$

$$H^+FeCl_4^- + CH_2 = CCl_2 \rightleftharpoons FeCl_4^-[CH_3C^{\oplus}Cl_2]$$

$$\downarrow\uparrow$$

$$FeCl_3 + CH_3CCl_3.$$

Scheme 5.I.

This, however, is inconsistent with the lack of exchange between anhydrous $FeCl_3$ and anhydrous HCl. Exchange takes place only when water is present which suggests that the catalytically active species is $[Fe(H_2O)_4Cl_2]^+$ which is formed in the hydrolysis of $FeCl_3$. When water is present in the reaction between

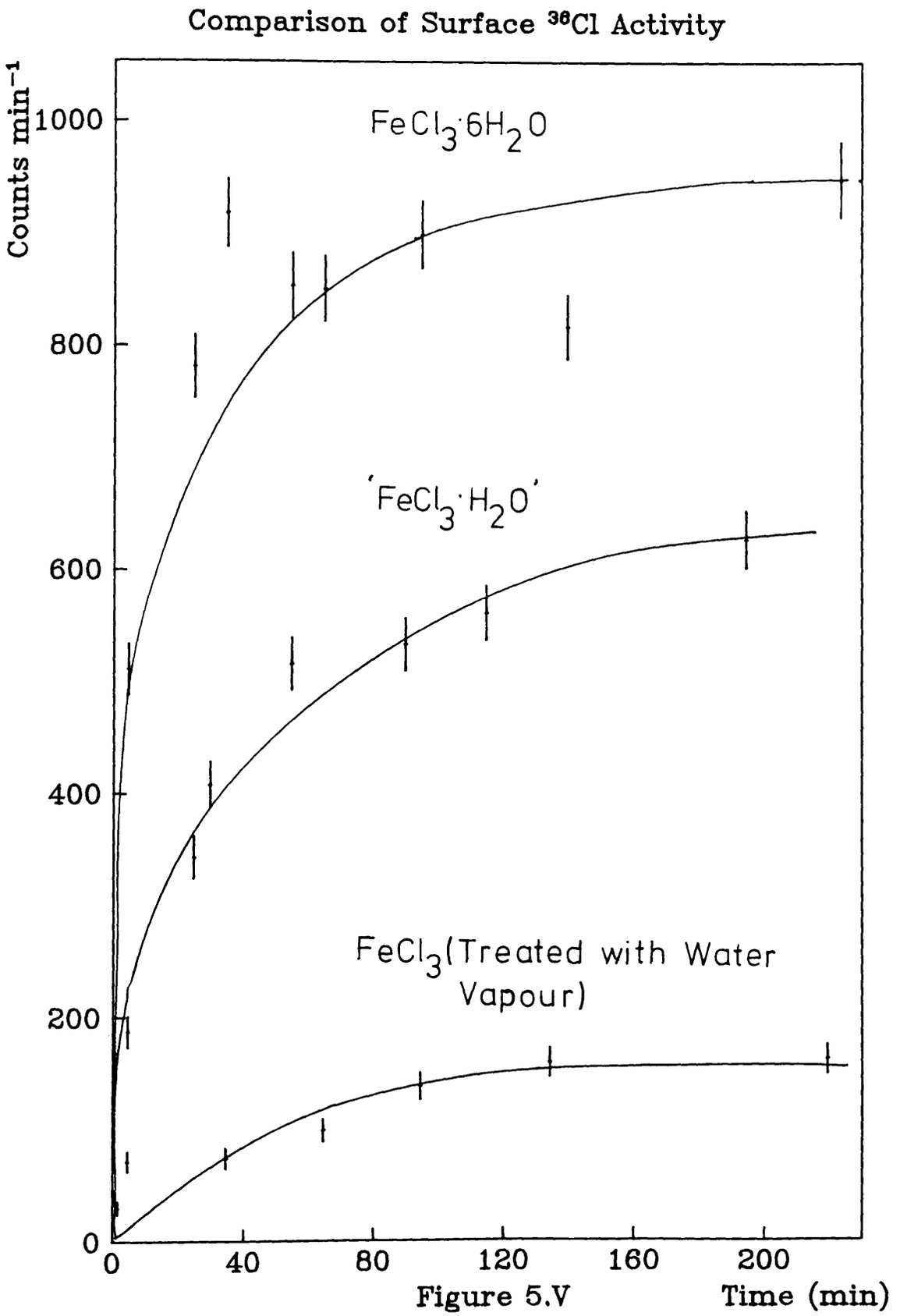

Comparison of Surface ^{36}Cl Activity
Counts min^{-1}
1000
800
600
400
200
0
$FeCl_3 \cdot 6H_2O$
'$FeCl_3 \cdot H_2O$'
$FeCl_3$(Treated with Water Vapour)
0
40
80
120
160
200
Time (min)

Figure 5.V

$FeCl_3$ and HCl, both exchange and adsorption occur. An alternative scheme for the hydrochlorination of vinylidene chloride by $FeCl_3$ could result from the adsorption of HCl by $[Fe(H_2O)_4Cl_2]^+$ weakening the H-Cl bond, thus causing slight ionization of HCl which results in protonation of vinylidene chloride with subsequent addition of a chloride ion giving 1,1,1-trichloroethane. This also explains the inhibition of hydrochlorination reactions in the presence of excess water since water is a better Lewis base than vinylidene chloride.

It is known when $FeCl_3$ is dissolved in other donor solvents, for example nitroalkane and nitrobenzene, that the rate of hydrochlorination increases (cf. 1.4.3). This is probably due to the solvolysis of molecular $FeCl_3$ giving the species $[Fe(L)_4Cl_2]^+$ which behaves in an analogous manner to $[Fe(H_2O)_4Cl_2]^+$.

These results show, therefore, that molecular $FeCl_3$ is not the catalytically active species in the hydrochlorination of chloroalkanes.

CHAPTER SIX

CHAPTER 6

INTERACTION OF IRON(III) CHLORIDE WITH 1,1,1-TRICHLOROETHANE

Iron(III) chloride can catalyse the dehydrochlorination of chloroethanes (cf. 1.4.4). To develop a better understanding of dehydrochlorination reactions the $FeCl_3$ - catalysed dehydrochlorination of 1,1,1-trichloroethane to give vinylidene chloride has been investigated. (Eq. 6.I).

$$CH_3CCl_3 \rightleftharpoons CH_2 = CCl_2 + HCl \qquad \text{.....Eq. 6.I}$$

The addition of anhydrous $FeCl_3$ to 1,1,1-trichloroethane must result in the production of HCl and vinylidene chloride. The factors which effect the production of vinylidene chloride were determined by adding HCl, water and acetonitrile to a mixture of $FeCl_3$ in 1,1,1-trichloroethane.

It has been suggested[5] that the dehydrochlorination mechanism involves a carbonium ion intermediate as shown in scheme 6.I and this would result in the

$$CH_3 - CCl_3 + FeCl_3 \rightarrow [CH_3CCl_2^+ + FeCl_4^-]$$

$$[CH_3CCl_2^+ + FeCl_4^-] \rightarrow CH_2CCl_2 + FeCl_3 + HCl$$

Scheme 6.I

tetrachloroferrate ion being observed in solution. UV spectra from the $FeCl_3|CH_3CCl_3$ system were examined for the presence of the $FeCl_4^-$ ion.

Since the dehydrochlorination of CH_3CCl_3 by $FeCl_3$ is an equilibrium reaction, the introduction of $H^{36}Cl$ to a mixture of $FeCl_3$ in CH_3CCl_3 should lead to incorporation of activity into $FeCl_3$ as shown in Scheme 6.II.

$$CH_3CCl_3 \rightleftharpoons CH_2 = CCl_2 + HCl$$

several times

$$H^{36}Cl + CH_2 = CCl_2 \rightleftharpoons CH_3C^{36}Cl_3$$

$$CH_3C^{36}Cl_3 + FeCl_3 \rightarrow [CH_3C^{36}Cl_2^+ + Fe^{36}Cl_4^-]$$

$$[CH_3C^{36}Cl_2^+ + Fe^{36}Cl_4^-] \rightarrow CH_2 = C^{36}Cl_2 + Fe^{36}Cl_3 + H^{36}Cl$$

Scheme 6.II

$H^{36}Cl$ was chosen to introduce the radiochemical label into the $FeCl_3|CH_3CCl_3$ system rather than $Fe^{36}Cl_3$ or $CH_3C^{36}Cl_3$ owing to the lack of a suitable radiochemical laboratory. It was not possible to prepare anhydrous $Fe^{36}Cl_3$ from the reaction with either $^{36}Cl_2$ or $H^{36}Cl$. Heating iron wire and $^{36}Cl_2$ in a Monel bomb did not produce a sufficient yield of active $FeCl_3$ to perform an exchange reaction. Active $FeCl_3$ could be produced in a similar way to inactive $FeCl_3$ as outlined in 2.2.1 but this requires a large fume hood built to radiochemical standards which was not available. To produce active CH_3CCl_3 requires GC facilities suitable for radiochemical work. $H^{36}Cl$ was therefore used in the exchange reactions performed.

Stabilizers, which amongst other things, inhibit the formation of HCl, are often added to CH_3CCl_3 for large scale use of this compound. Reactions were performed using both unstabilized and stabilized 1,1,1-trichloroethane.

6.1. EXPERIMENTAL

6.1.1. IR ANALYSIS OF THE VAPOUR FROM THE $FeCl_3|CH_3CCl_3$ SYSTEM.

A rotaflo vessel was pumped and flamed out before being transferred to an inert atmosphere box. A mixture of $FeCl_3$ in CH_3CCl_3 was prepared in the box by weighing $FeCl_3$ (0.1543g; 0.95 mmol) into the rotaflo vessel and adding 25ml of CH_3CCl_3. The $FeCl_3$ did not dissolve completely and the orange-brown solution contained some undissolved solid. The vessel was removed from the box and the mixture degassed twice. The vapour from this reaction was monitored by expanding the vapour into the vacuum manifold, which contained a gas infrared cell, and recording its infrared spectrum. Vapour pressures obtained were measured using a mercury manometer and were in the range 150 - 190 mm Hg. The HCl was detected by its characteristic bands at 3050 cm^{-1} -2650 cm^{-1}.

6.1.2. G.L.C. AND Fe^{II} ANALYSIS OF THE $FeCl_3|CH_3CCl_3$ SYSTEM.

Twenty identical solutions of $FeCl_3$ in CH_3CCl_3 were prepared in the inert atmosphere box by weighing

$FeCl_3$ (0.0324g; 0.20 mmol) into a rotaflo vessel and adding 10 ml of CH_3CCl_3. The $FeCl_3$ did not dissolve completely in CH_3CCl_3. These mixtures were transferred to the vacuum line and degassed twice. The mixtures were used to determine the effect of adding HCl, H_2O or CH_3CN on the production of vinylidene chloride and Fe^{II} and these reagents were added to selected solutions as shown in Table 6.I. In two cases, solutions were stored in the dark so that any photochemical contribution to the formation of Fe^{II} and vinylidene chloride could be determined. The Fe^{II} analyses were performed as outlined in section 2.3.3 and G.L.C. measurements were carried out under the conditions shown in Table 6.II using a calibration curve constructed for vinylidene chloride in CH_3CCl_3. (Figure 6.I). Toluene was used as the internal standard as outlined in section 2.7.

6.1.3. ELECTRONIC SPECTRA OF $FeCl_3|CH_3CCl_3$, $FeCl_3|CH_3CCl_3|$ HCl AND $FeCl_3|CH_3CCl_3|HCl|H_2O$.

Three UV cells were pumped and flamed out before being transferred to the inert atmosphere box. A mixture of $FeCl_3$ in CH_3CCl_3 was prepared by weighing $FeCl_3$ (0.0324g; 0.20 mmol) into each UV cell and adding 5 ml of CH_3CCl_3. The UV cells were transferred to the vacuum line and the mixtures degassed twice. A weighed amount of HCl (0.0288g; 0.79 mmol) was

AMOUNTS OF HCl, H_2O AND CH_3CN ADDED TO THE $FeCl_3$ | CH_3CCl_3 SYSTEM.

AMOUNTS OF HCl, H_2O AND CH_3CN ADDED TO THE $FeCl_3$ | CH_3CCl_3 SYSTEM.

Sample	Added Water mmol.	Added HCl. mmol.	Added CH_3CN mmol.	Time
1A	-	-	-	6 days
1B	-	1.38	-	6 days
2A	-	-	-	4 days
2B	-	1.01	-	4 days
3A	-	-	-	2 days
3B	-	1.09	-	2 days
4A	-	-	-	1 day
4B	-	1.12	-	1 day
5A	-	-	-	3h.
5B	-	1.14	-	3h.
M	0.088	1.19	-	3h.
Q	0.088	1.56	-	1 day
P	0.066	1.44	-	2 days
O	0.077	0.95	-	4 days
N	0.079	1.24	-	6 days
* R	-	-	-	1 day
* S	-	-	-	5 days
V	-	0.96	3.83	2 days
U	-	1.20	3.83	3 days
T	-	0.54	3.83	5 days

* Solutions Stored in the Dark.

TABLE 6.I.

GLC ANALYSIS CONDITIONS

Performed On	Carlo Erba Capillary GC Unit Fractovap 2351AC
Column	50 m Carbowax 20M on Glass
Temperature	81°C
Carrier Gas	Helium
Carrier Flow	1ml min^{-1}
Split Mode	50/1 (1 through column)
Injection Size	10µl
Internal Standard	100µl Toluene (AR) TO 50ml sample.

TABLE 6.II

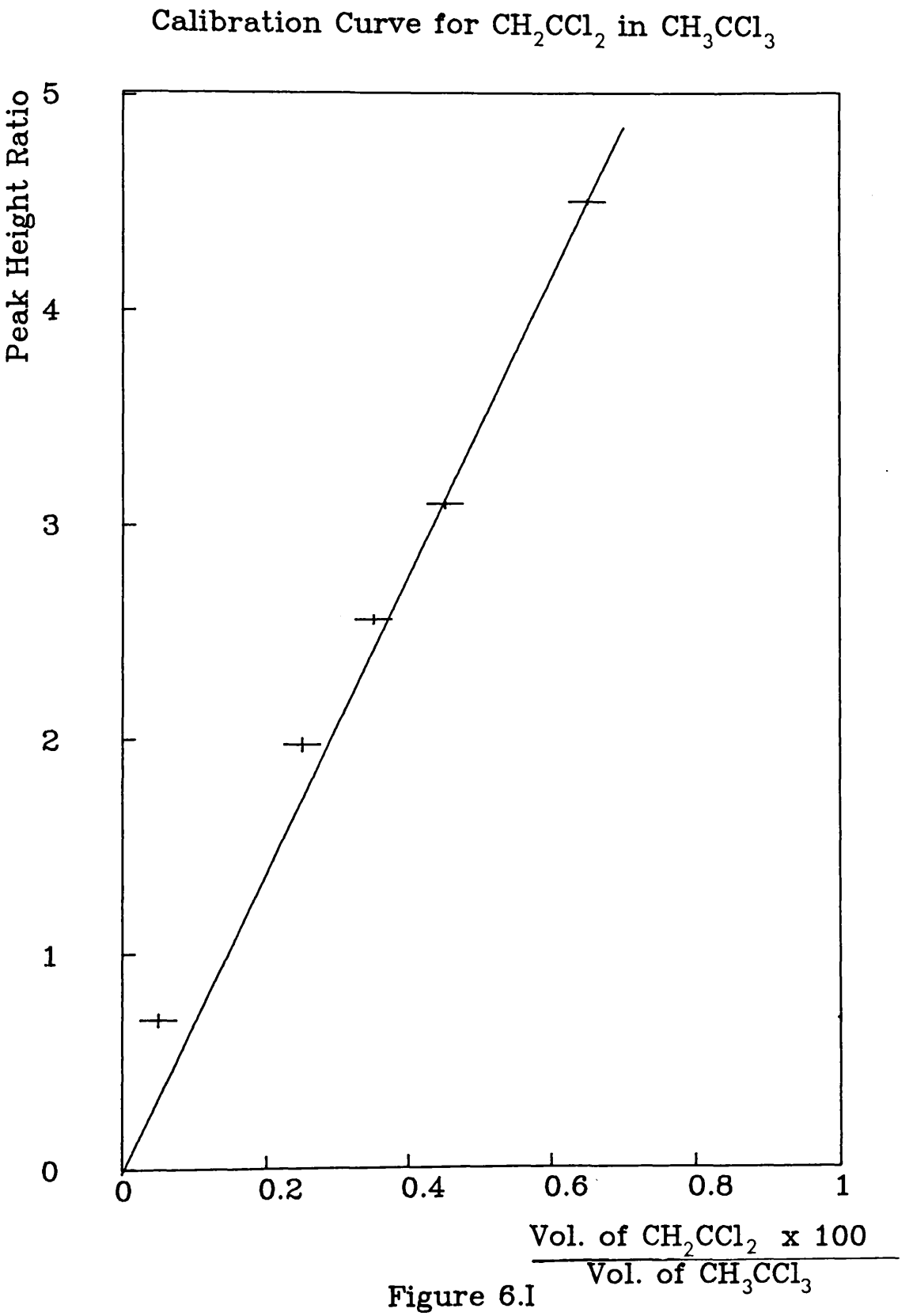

Calibration Curve for CH_2CCl_2 in CH_3CCl_3
Peak Height Ratio
0
1
2
3
4
5
0
0.2
0.4
0.6
0.8
1
Vol. of CH_2CCl_2 x 100
Vol. of CH_3CCl_3

Figure 6.I

added to one of the UV cells by holding the mixture of $FeCl_3$ in CH_3CCl_3 at 77K and distilling the HCl into the cell. A flask containing distilled water (T. = 297K, V.P. = 22.377 mm Hg) was attached to the vacuum line and the system pumped for several hours before the flask was opened and the vapour allowed to expand into the manifold which contained an empty rotaflo vessel (vol = 65.23 ml). After 10 minutes, the rotaflo vessel was closed, the distilled water removed from the line and the system pumped. The water vapour (0.0014g; 0.079 mmol) contained in this vessel was transferred under vacuum into one of the $FeCl_3|CH_3CCl_3$ mixtures and a weighed amount of HCl (0.0205g; 0.56 mmol) then added to this mixture. Electronic spectra of the three mixtures were recorded at intervals over three weeks.

6.1.4. INTERACTION OF $FeCl_3$ WITH CH_3CCl_3 AND $H^{36}Cl$ MONITORED BY EXCHANGE METHOD A.

This reaction was performed using exchange method A (cf. 2.6.1). Iron(III) chloride (0.2899g; 1.79 mmol) was weighed in a previously flamed-out reaction vessel in the inert atmosphere box. The flask containing the $FeCl_3$ was removed and evacuated before being attached to the counting vessel shown in Figure 2XV. The system was pumped for several hours before the $FeCl_3$ was admitted to the movable boat and placed directly under one of the GM tubes.

1,1,1-Trichloroethane was purified as outlined in 2.4.3. and transferred to the inert atmosphere box where it was placed in a previously flamed-out rotaflo vessel. It was transferred to a vacuum line and degassed twice. Vessel V_1 (Vol. = 551.9ml) was attached to the vacuum line and evacuated. The flask containing CH_3CCl_3 was opened and the vapour allowed to expand into V_1 (Temperature = 298K, V.P. = 127 mm Hg). Vessel V_1, therefore, contained 3.77 mmol of CH_3CCl_3.

A bulb (Vol. = 124.6 ml) was evacuated and weighed before the addition of anhydrous $H^{36}Cl$. The specific activity of the $H^{36}Cl$ had been determined and was 788 ± 34 counts $(5min)^{-1}$ mg^{-1}. The $H^{36}Cl$ (0.1692g; 4.64 mmol) was then vacuum distilled at 77K into vessel V_1, which contained the CH_3CCl_3. The vessel was then attached to the vacuum line (Figure 2.XV) and the system pumped overnight. Tap C was closed and the mixture of $H^{36}Cl$ and CH_3CCl_3 admitted to the reaction vessel, which was isolated from the rest of the system by closing tap B. The amount of $H^{36}Cl$ in the counting vessel and in contact with $FeCl_3$ was 0.0783g; 2.15 mmol and the amount of CH_3CCl_3 was 0.2327g; 1.74 mmol . The counts from both tubes were monitored for 2h. (Table 6.III). After 2h the $CH_3CCl_3|H^{36}Cl$ mixture was removed by vacuum distillation. The mixture was separated by fractional distillation from 188K to 77K,

INTERACTION BETWEEN $FeCl_3$|CH_3CCl_3|$H^{36}Cl$:- EXCHANGE METHOD A.

	Counts min^{-1} in → Solid & Gas Phases	-Background →	Counts min^{-1} Corrected for Dead Time	Counts min^{-1} in → Gas Phase	-Background →	Counts min^{-1} Corrected for Dead Time	Tubes Inter-calibrated	Surface Activity of FeCl Counts min^{-1}	Time Min.
	1407	1243	1251	1234	1044	1049	1248	3	5
*	14321	12681	12762	12573	10673	10731	12770	-8	10
	1434	1270	1278	1241	1051	1057	1257	21	25
*	14298	12658	12739	12391	10491	10546	12547	192	30
	1426	1262	1270	1212	1023	1028	1223	47	45
*	14321	12681	12762	12124	10224	10276	12226	536	50
	1454	1290	1298	1222	1033	1038	1235	63	70
*	14559	12919	13003	12164	10264	10317	12274	729	75
	1467	1303	1312	1221	1031	1036	1233	79	85
	1471	1307	1316	1220	1030	1035	1232	84	90
*	14714	13074	13160	12098	10198	10250	12195	965	95
	1473	1309	1318	1207	1017	1022	1216	102	120

* Counts for 10 min.

TABLE 6.III

$H^{36}Cl$ being recovered from the 77K fraction. The $H^{36}Cl$ was then distilled into a frozen solution of NaOH, $^{36}Cl^-$ precipitated as $Ag^{36}Cl$ and its activity determined. (Table 6.IV). The $FeCl_3$ was analysed by hydrolysing the sample, precipitating the iron as Fe_2O_3 and the Cl^- as AgCl. (Table 6.V). The $FeCl_3$ was found to be inactive (Table 6.IV).

ANALYSIS OF $FeCl_3$ FROM THE INTERACTION OF $FeCl_3$ WITH CH_3CCl_3 AND $H^{36}Cl$ MONITORED BY EXCHANGE METHOD A.

	% Obtained	% Required for $FeCl_3$
Iron	34.2	34.4
Chlorine	65.1	65.6

TABLE 6.V

6.1.5. INTERACTION OF $FeCl_3$ (TREATED WITH WATER VAPOUR) WITH CH_3CCl_3 AND $H^{36}Cl$ MONITORED BY EXCHANGE METHOD A.

Iron(III) chloride (0.3469g; 2.14 mmol) was placed under a GM tube as outlined in 6.1.4. A flask containing distilled water (Temp.= 298K, V.P. = 23.756 mm Hg) was attached to the line at V_1 and the system pumped for several hours. The flask was opened and the water vapour left in contact with the $FeCl_3$ for 3h. After this time,

SPECIFIC ACTIVITIES FROM $FeCl_3|CH_3CCl_3|H^{36}Cl$:- EXCHANGE METHOD A

Sample	(1) Amount of $Ag^{36}Cl$ Counted mg	(1) Counts(5min)$^{-1}$ * ±	(1) Counts(5min)$^{-1}$ mg^{-1} ±	(1) Counts(5min)$^{-1}$ mg^{-1} Corrected for Self-Absorption	(2) Amount of $Ag^{36}Cl$ Counted mg ±	(2) Counts(5min)$^{-1}$ * ±	Counts(5min)$^{-1}$ mg^{-1} ±	Counts(5min)$^{-1}$ mg^{-1} Corrected for Self-Absorption	Average Specific Activity$_1$ Counts(5min)$^{-1}$ mg^{-1}
Initial $H^{36}Cl$	16.9	12108	716	784	17.5	12355	706	792	788 ± 34
Final $H^{36}Cl$	15.9	8793	553	575	16.3	8913	547	583	579 ± 27
$FeCl_3$.	17.2	None Observed	-	Sample Inactive	15.4	None Observed	-	Sample Inactive	Sample Inactive

* Counts Corrected for Dead Time and Background

TABLE 6.IV

the remaining H_2O vapour was removed by pumping. Tap B was then closed and the flask containing the distilled water removed. Flask V_1, which contained anhydrous $H^{36}Cl$ (0.1872g; 5.13 mmol) and CH_3CCl_3 (0.5042g; 3.77 mmol) prepared as described in 6.1.4, was attached to the line and the system pumped for several hours. $H^{36}Cl$ (0.0865g; 2.37 mmol in the reaction vessel) and CH_3CCl_3 (0.2327g; 1.74 mmol in the reaction vessel) were admitted to the $FeCl_3$ and the system monitored for 2h. (Table 6.VI). The $CH_3CCl_3|H^{36}Cl$ mixture was removed by vacuum distillation at 77K. The mixture was separated, the $H^{36}Cl$ distilled into a frozen solution of NaOH, precipitated as $Ag^{36}Cl$ and its activity determined. (Table 6.VII). The $FeCl_3$ was analysed by hydrolysing the sample, precipitating the iron as Fe_2O_3 and the $^{36}Cl^-$ as $Ag^{36}Cl$ (Table 6.VIII). The activity of the $FeCl_3$ was determined as $Ag^{36}Cl$ (Table 6.VII).

ANALYSIS OF $FeCl_3$ FROM THE INTERACTION OF $FeCl_3$ (WATER VAPOUR) WITH CH_3CCl_3 and $H^{36}Cl$.

	% Obtained	% Required for $FeCl_3$
Iron	34.2	34.4
Chlorine	65.1	65.6

TABLE 6.VIII

INTERACTION BETWEEN $FeCl_3$ (TREATED WITH WATER VAPOUR)|CH_3CCl_3|$H^{36}Cl$.

	Counts min^{-1} in Solid & Gas Phases ↓	-Background ↓	Counts min^{-1} Corrected for Dead Time	Counts min^{-1} in Gas Phase ↓	-Background ↓	Counts min^{-1} Corrected for Dead Time	Surface Activity of $FeCl_3$ Counts min^{-1}	Time Min
	1475	1305	1314	1447	1253	1261	53	0
	1593	1423	1433	1381	1187	1194	239	5
*	20044	18344	18514	13006	11066	11127	7387	10
	2239	2069	2084	1214	1020	1025	1059	25
*	22316	20616	20830	12228	10288	10341	10488	30
	2252	2082	2097	1169	975	980	1117	45
*	22676	20976	21198	11534	9594	9640	11558	50
	2272	2102	2117	1148	954	959	1158	70
*	22510	20810	21029	11517	9577	9623	11406	75
	2152	1982	1996	1127	983	938	1058	90
*	21592	19892	20092	11281	9341	9385	10707	95
	2110	1940	1954	1103	909	913	1041	105
	2187	2017	2031	1094	900	904	1127	120

* Counts for 10 min.

TABLE 6.VI

SPECIFIC ACTIVITIES FROM $FeCl_3$ (TREATED WITH WATER VAPOUR) CH_3CCl_3 | $H^{36}Cl$.

Sample	(1) Amount of $Ag^{36}Cl$ Counted mg	(1) Counts(5min)$^{-1}$ * +	(1) Counts(5min)$^{-1}$ mg^{-1} +	(1) Counts(5min)$^{-1}$ mg^{-1} Corrected for Self-Absorption	(2) Amount of $Ag^{36}Cl$ Counted mg +	(2) Counts(5min)$^{-1}$ * +	Counts(5min)$^{-1}$ mg^{-1} +	Counts(5min)$^{-1}$ mg^{-1} Corrected for Self-Absorption	Average Specific Activity $_1$ Counts(5min)$^{-1}$ mg^{-1}
Initial $H^{36}Cl$	15.4	12613	819	835	15.9	13006	818	851	843 ± 40
Final $H^{36}Cl$	17.5	9782	559	627	16.3	9405	577	615	621 ± 28
$FeCl_3$.	14.8	444	30	30	22.4	591	26	36	33 ± 3

* Counts Corrected for Dead Time

TABLE 6.VII

6.1.6. INTERACTION OF $FeCl_3$ WITH CH_3CCl_3 AND $H^{36}Cl$ MONITORED BY EXCHANGE METHOD B.

The reaction was performed using exchange method B (cf. 2.6.2) and the apparatus shown in Figure 2.XVIII. This apparatus was pumped and flamed-out on a vacuum line before being transferred to the inert atmosphere box. A mixture of $FeCl_3$ in CH_3CCl_3 was prepared by weighing $FeCl_3$ (0.1000g; 0.62 mmol) into V_1 of the exchange vessel and adding 50ml of CH_3CCl_3. The vessel was removed from the dry box and the mixture degassed twice before a weighed amount of $H^{36}Cl$ (0.2196g; 6.02 mmol) was added. The specific activity of a sample of the $H^{36}Cl$ used was determined before the addition. The exchange vessel was thermostated at 298K. At intervals the exchange vessel was attached to the vacuum line and the $FeCl_3|CH_3CCl_3$ mixture held at 188K. The $H^{36}Cl$ was removed by allowing the gas into V_2. The $H^{36}Cl$ was then distilled into a frozen solution of NaOH, precipitated as $Ag^{36}Cl$ and its specific activity determined. (Table 6.IX). After the removal of all the $H^{36}Cl$, the solvent was removed by vacuum distillation and the $FeCl_3$ analysed by hydrolysing the sample, precipitating the iron as Fe_2O_3 and the chloride ion as AgCl. (Table 6.X). The $FeCl_3$ was found to be inactive. (Table 6.IX).

INTERACTION BETWEEN $FeCl_3$|CH_3CCl_3|$H^{36}Cl$:- EXCHANGE METHOD B

Sample	Time	Amount AgCl Counted mg	Corrected Count* Counts(10min)$^{-1}$	Counts(10min)$^{-1}$ mg^{-1}	Corrected for Self-Absorption	Amount AgCl Counted mg	Corrected Count* Counts(10min)$^{-1}$	Counts(10min)$^{-1}$ mg^{-1}	Corrected for Self-Absorption	Average Count Counts(10min)$^{-1}$mg^{-1}
Initial	0	14.3	6514	455	443	20.6	7694	373	470	456
1st	3h	16.3	742	45.5	48.6	24.8	980	39.5	57.2	52.9
2nd	6h	16.0	179	11.2	11.8	16.3	183	11.2	12.0	11.9
3rd	24h	16.7	86	5.15	5.62	16.9	92	5.4	6.01	5.7
4th	48h	23.6	94	3.98	5.56	17.7	139	7.8	8.8	7.18
$FeCl_3$	After solvent Removed	20.8	-	-	-	21.1	-	-	-	-

* Corrected for Background and Dead Time

TABLE 6.IX

ANALYSIS OF $FeCl_3$ FROM THE INTERACTION OF $FeCl_3$ WITH CH_3CCl_3 AND $H^{36}Cl$ MONITORED BY EXCHANGE METHOD B.

	% Obtained	% Required for $FeCl_3$
Iron	33.8	34.4
Chlorine	64.9	65.6

TABLE 6.X

6.1.7. IR ANALYSIS OF THE VAPOUR FROM $FeCl_3$ AND STABILIZED CH_3CCl_3.

A rotaflo vessel was pumped, flamed out and transferred to the inert atmosphere box. A mixture of $FeCl_3$ in stabilized CH_3CCl_3 was prepared in the box by weighing $FeCl_3$ (0.1120g; 0.69 mmol) into a rotaflo vessel and adding 50ml of stabilized CH_3CCl_3. The $FeCl_3$ did not completely dissolve in this solvent. The vessel was removed from the box and the mixture degassed twice. The vapour from this reaction was monitored regularly over a three week period by expanding the vapour into the vacuum manifold, which contained a gas infrared cell, and recording its infrared spectrum. Vapour pressures obtained were measured using a mercury manometer and were in the range 91 - 106 mm Hg.

6.1.8. G.L.C. AND Fe^{II} ANALYSIS OF $FeCl_3$|STABILIZED CH_3CCl_3 AND $FeCl_3$|STABILIZED CH_3CCl_3|HCl.

Two rotaflo vessels were pumped, flamed out and transferred to the inert atmosphere box. Two mixtures of $FeCl_3$ in stabilized CH_3CCl_3 were prepared in the box by weighing $FeCl_3$ (0.1120g; 0.69 mmol) into each rotaflo vessel and adding 50ml of stabilized CH_3CCl_3. The $FeCl_3$ did not completely dissolve in stabilized CH_3CCl_3. The rotaflo vessels were transferred to the vacuum line and the mixtures degassed twice. A weighed amount of HCl (0.1480g; 4.06 mmol) was added to one of the rotaflo vessels by holding the mixture of $FeCl_3$ in stabilized CH_3CCl_3 at 77K and distilling the HCl into the vessel. After three weeks both solutions were yellow-green and contained no undissolved solid. The solvent was removed and examined by GLC and the solid remaining was analysed for Fe^{II} and total iron as described in section 2.3.3.

6.1.9. ELECTRONIC SPECTRA OF $FeCl_3$|STABILIZED CH_3CCl_3 AND $FeCl_3$|STABILIZED CH_3CCl_3|HCl.

Two UV cells were pumped, flamed-out and transferred to the inert atmosphere box. A mixture of $FeCl_3$ in stabilized CH_3CCl_3 was prepared by weighing $FeCl_3$ (0.0324g; 0.2 mmol) into each UV cell and adding 5ml of stabilized CH_3CCl_3. The UV cells were transferred to

the vacuum line and the mixture degassed twice. The $FeCl_3$ did not dissolve completely in stabilized CH_3CCl_3. A weighed amount of HCl (0.0312g; 0.86 mmol) was added to one of the UV cells by vacuum distillation. The electronic spectra of both mixtures were monitored over three weeks and after this time all the $FeCl_3$ has dissolved.

6.1.10. INTERACTION OF $FeCl_3$ WITH STABILIZED CH_3CCl_3 AND $H^{36}Cl$ MONITORED BY EXCHANGE METHOD A.

The reaction between $FeCl_3$ (0.1630g; 1.01 mmol), $H^{36}Cl$ (0.0887g; 2.43 mmol in the reaction vessel) and stabilized CH_3CCl_3 (0.2327g; 1.74 mmol in the reaction vessel) was performed as described in section 6.1.4. and the system monitored for 2.83h (Table 6.XI). After 2.83h the $H^{36}Cl$|stabilized CH_3CCl_3 mixture was removed by vacuum distillation. The mixture was separated by fractional distillation from 188K to 77K, $H^{36}Cl$ being recovered from the 77K fraction. The $H^{36}Cl$ was then distilled into a frozen solution of NaOH, $^{36}Cl^-$ precipitated as $Ag^{36}Cl$ and its activity determined. (Table 6.XII). The solid remaining was analysed after hydrolysis by precipitating the iron as Fe_2O_3 and the chloride ion as $Ag^{36}Cl$ (Table 6.XIII). The activity of the solid was determined as $Ag^{36}Cl$. (Table 6.XII).

INTERACTION BETWEEN $FeCl_3$ | STABILIZED CH_3CCl_3 :- EXCHANGE METHOD A.

Counts min^{-1} in Solid & Gas Phases +	-Background +	Counts min^{-1} Corrected for Dead Time	Counts min^{-1} in Gas Phase +	-Background +	Counts min^{-1} Corrected for Dead Time	Surface Activity of $FeCl_3$ Counts min^{-1}	Time Min
1470	1413	1423	1470	1413	1423	0	0
1872	1815	1832	1335	1278	1286	546	2
2043	1986	2006	1271	1214	1221	785	6
2321	2264	2290	1266	1209	1216	1074	15
2148	2091	2113	1248	1191	1198	915	25
2353	2296	2323	1187	1130	1136	1187	35
2788	2731	2769	1132	1075	1081	1688	75
2586	2529	2561	1091	1035	1039	1522	95
2601	2544	2577	1098	1041	1046	1531	110
2673	2616	2651	1074	1017	1022	1629	170

TABLE 6.XI

SPECIFIC ACTIVITIES FROM $FeCl_3$ | STABILISED CH_3CCl_3:- EXCHANGE METHOD A.

Sample	(1) Amount of $Ag^{36}Cl$ Counted mg	(1) Counts(5min)$^{-1}$ * +	(1) Counts(5min)$^{-1}$ mg^{-1} +	(1) Counts(5min)$^{-1}$ mg^{-1} Corrected for Self-Absorption	(2) Amount of $Ag^{36}Cl$ Counted mg +	(2) Counts(5min)$^{-1}$ * +	Counts(5min)$^{-1}$ mg^{-1} +	Counts(5min)$^{-1}$ mg^{-1} Corrected for Self-Absorption	Average Specific Activity Counts(5min)$^{-1}$ mg^{-1}
Initial $H^{36}Cl$	13.2	2049	155	144	17.0	2346	138	152	154 ± 8
Final $H^{36}Cl$	16.0	1920	120	123	18.8	2068	110	129	126 ± 6
Remaining Solid After Solvent Removed	24.9	307	12	18	22.0	346	16	21	20 ± 2

* Counts Corrected for Dead Time and Background

TABLE 6.XII

ANALYSIS OF THE REMAINING SOLID FROM THE INTERACTION OF $FeCl_3$ WITH STABILIZED CH_3CCl_3 AND $H^{36}Cl$.

	Amount Obtained g	Amount Required for $FeCl_3$ Used g
Iron	0.0554	0.0561
Chlorine	0.1258	0.1069

TABLE 6.XIII

6.1.11. INTERACTION OF $FeCl_3$ WITH STABILIZED CH_3CCl_3 AND $H^{36}Cl$ MONITORED BY EXCHANGE METHOD B.

The reaction between a mixture of $FeCl_3$ (0.1622g; 1.00 mmol) in 50ml of stabilized CH_3CCl_3 and $H^{36}Cl$ (0.2847g; 7.81 mmol) was performed as described in section 6.1.6. After 1h the amount of $H^{36}Cl$ which could be removed from the $FeCl_3$|stabilized CH_3CCl_3 mixture was too small to count accurately and after a further 3h, no $H^{36}Cl$ could be removed. After 48h, the solvent was removed by vacuum distillation and the solid remaining was analysed by hydrolysing the sample, precipitating the iron as Fe_2O_3 and the chloride ion as $Ag^{36}Cl$. (Table6.XIV). The ^{36}Cl specific activity of the solid was determined as $Ag^{36}Cl$ (Table 6.XV).

SPECIFIC ACTIVITIES FROM $FeCl_3$ | STABILIZED CH_3CCl_3:- EXCHANGE METHOD B.

Sample	(1) Amount of $Ag^{36}Cl$ Counted mg	(1) Counts(5min)$^{-1}$ * ±	(1) Counts(5min)$^{-1}$mg^{-1} ±	(1) Counts(5min)$^{-1}$mg^{-1} Corrected for Self-Absorption	(2) Amount of $Ag^{36}Cl$ Counted ±	(2) Counts(5min)$^{-1}$ * ±	Counts(5min)$^{-1}$mg^{-1} ±	Counts(5min)$^{-1}$mg^{-1} Corrected for Self-Absorption	Average Specific Activity Counts(5min)$^{-1}$mg^{-1}
Initial $H^{36}Cl$	15.6	1287	82	84	14.1	1362	96	94	89 ± 6
Remaining Solid After Solvent Removed	15.8	1194	78	79	18.7	1401	75	88	84 ± 4

* Counts corrected for Dead Time and Background.

TABLE 6.XV

ANALYSIS OF THE REMAINING SOLID FROM THE INTERACTION OF $FeCl_3$ WITH STABILIZED CH_3CCl_3 AND $H^{36}Cl$.

	Amount Obtained g	Amount Required for $FeCl_3$ Used g
Iron	0.0483	0.0558
Chlorine	0.1403	0.1064

TABLE 6.XIV

6.2. RESULTS

6.2.1. INTERACTION OF $FeCl_3$ WITH CH_3CCl_3.

$FeCl_3$ does not dissolve completely in CH_3CCl_3 but forms an orange-brown solution which contains some undissolved solid. Infrared spectra of the vapour from a mixture of $FeCl_3$ (0.1543g; 0.95 mmol) in 25ml of CH_3CCl_3 show that HCl is present after 30min. which indicates that $FeCl_3$ is catalysing the dehydrochlorination of CH_3CCl_3. GLC analysis confirms that vinylidene chloride is formed when $FeCl_3$ is added to CH_3CCl_3.

6.2.2. GLC AND Fe^{II} ANALYSIS OF THE $FeCl_3|CH_3CCl_3$ SYSTEM.

The effect on the production of vinylidene chloride and Fe^{II} of adding HCl, H_2O or CH_3CN was determined by adding these reagents to selected solutions of $FeCl_3$ (0.0324g; 0.20 mmol) in CH_3CCl_3 (10ml). In two cases solutions were stored in the dark so that any photochemical contribution to the formation of Fe^{II} and vinylidene chloride could be determined. The results are shown in Table 6.XVI. Samples 1A → 5A and 1B → 5B were prepared under identical conditions though HCl was added to samples 1B → 5B. The addition of HCl decreases the amount of vinylidene chloride formed but has no effect on the amount of iron present as Fe^{II}. Samples 5A and 5B, which were examined after only 3h, show that less vinylidene chloride and Fe^{II} are present than in samples 4A and 4B which were examined after 1 day. Samples which were left for longer than 1 day show very little change in the amount of vinylidene chloride and Fe^{II} formed. The addition of water to samples M → N reduces both the amount of vinylidene chloride and Fe^{II} formed. The addition of CH_3CN to samples V → T stops the formation of vinylidene chloride but has no effect on the amount of Fe^{II} produced. Samples R and S were stored in the dark and show a vast increase in the amount of vinylidene chloride formed compared to the samples stored in the light. In both solutions stored in the dark the production of Fe^{II} is totally inhibited.

EFFECT OF ADDING HCl, H_2O AND CH_3CN ON THE $FeCl_3|CH_3CCl_3$ SYSTEM.

	Sample	Added Water mmol.	Added HCl mmol	Added CH_3CN mmol	Time	Amount of Vinylidene Chloride Present mol l^{-1}	%Fe^{II} Present of Total Iron
	1A	-	-	-	6 days	0.1250	24
	1B	-	1.38	-	6 days	0.0707	28
	2A	-	-	-	4 days	0.0631	28
	2B	-	1.01	-	4 days	0.0569	24
	3A	-	-	-	2 days	0.0767	24
	3B	-	1.09		2 days	0.0726	22
	4A	-	-	-	1 day	0.0842	16
	4B	-	1.12	-	1 day	0.0413	24
	5A	-	-	-	3h.	0.0179	8
	5B	-	1.14	-	3h.	0.0132	10
	M	0.088	1.19	-	3h.	0.0129	0.8
	Q	0.088	1.56	-	1 day	0.0452	21
	P	0.066	1.44	-	2 days	0.0279	19
	O	0.077	0.95	-	4 days	0.0394	16
	N	0.079	1.24	-	6 days	0.0432	20
*	R	-	-	-	1 day	0.109	None Detected
*	S	-	-	-	5 days	2.25	None Detected
	V	-	0.96	3.83	2 days	None Detected	24
	U	-	1.20	3.83	3 days	None Detected	25
	T	-	0.54	3.83	5 days	None Detected	28

* Solutions stored in the dark.

TABLE 6.XVI

6.2.3. ELECTRONIC SPECTRA OF $FeCl_3|CH_3CCl_3$, $FeCl_3|CH_3CCl_3|HCl$ AND $FeCl_3|CH_3CCl_3|HCl|H_2O$.

The electronic spectra of the three systems, $FeCl_3|CH_3CCl_3$, $FeCl_3|CH_3CCl_3|HCl$ and $FeCl_3|CH_3CCl_3|HCl|H_2O$, were recorded over a period of time. Spectroscopic examination of the $FeCl_3|CH_3CCl_3$ and $FeCl_3|CH_3CCl_3|HCl$ systems in the region 12500 cm^{-1} to 22000 cm^{-1} shows no evidence for the formation of the tetrachloroferrate ion even after three weeks. In the $FeCl_3|CH_3CCl_3|HCl|H_2O$ system, bands at 16400 cm^{-1}, 18900 cm^{-1}, and 20400 cm^{-1} (cf. Table 4.XXXVII) indicate that the $FeCl_4^-$ ion is present in solution after 4h.

6.2.4. INTERACTION OF $FeCl_3$ WITH CH_3CCl_3 AND $H^{36}Cl$ MONITORED BY EXCHANGE METHOD A.

When $H^{36}Cl$ (0.0783g; 2.15 mmol) and CH_3CCl_3 (0.2327g; 1.74 mmol) are admitted to $FeCl_3$ (0.2899g; 1.79 mmol) and the resulting distribution of ^{36}Cl activity monitored by two GM tubes, the count rate from the gas plus solid increases with time and that from the gas alone decreases. The surface activity of $FeCl_3$ is decreased by the removal of the $H^{36}Cl|CH_3CCl_3$ mixture and totally removed by overnight pumping. Analysis of the $FeCl_3$ indicates that the ratio Fe:Cl is 1:3.0 and that $FeCl_3$ is inactive (Table 6.IV).

This shows that no exchange has occurred between $FeCl_3$ and the $H^{36}Cl|CH_3CCl_3$ mixture. Previous results have shown that $H^{36}Cl$ is not adsorbed by $FeCl_3$ so the surface activity exhibited by the $FeCl_3$ in this reaction is probably due to either $CH_3C^{36}Cl_3$ or $CH_2 = C^{36}Cl_2$ being adsorbed by the $FeCl_3$. ^{36}Cl activity would be incorporated into both $CH_3C^{36}Cl_3$ and $CH_2 = C^{36}Cl_2$ as shown in scheme 6.II. Analysis of the $H^{36}Cl$, before and after the reaction shows a decrease in the specific activity of the $H^{36}Cl$. (Table 6.XVII). This is probably due to the formation of inactive HCl produced by the dehydrochlorination of CH_3CCl_3 by $FeCl_3$.

SPECIFIC ACTIVITIES OF THE REACTANTS FROM THE INTERACTION OF $FeCl_3$ WITH CH_3CCl_3 AND $H^{36}Cl$.

Sample	Specific Activity Counts $(5min)^{-1}mg^{-1}$
Initial $H^{36}Cl$, counted as $Ag^{36}Cl$	788 ± 34
Final $H^{36}Cl$, counted as $Ag^{36}Cl$	579 ± 27
$FeCl_3$ counted as AgCl	Not active

TABLE 6.XVII

6.2.5. INTERACTION OF $FeCl_3$ (TREATED WITH WATER VAPOUR) WITH CH_3CCl_3 AND $H^{36}Cl$ MONITORED BY EXCHANGE METHOD A.

Examination of the ^{36}Cl activity distribution in the heterogeneous system when $H^{36}Cl$ (0.0865g; 2.37 mmol) and CH_3CCl_3 (0.2327g; 1.74 mmol) are admitted to $FeCl_3$ (0.3469g; 2.14 mmol), which has been treated previously with water vapour, indicates that the count rate from the gas plus solid increases with time while that of the gas alone decreases. The variation of the surface ^{36}Cl activity of $FeCl_3$ with time is shown in Figure 6.II. The surface activity is unaffected by the removal of $H^{36}Cl$ and CH_3CCl_3 though it decreases slightly after pumping overnight. Analysis of the $FeCl_3$ after $H^{36}Cl$ and CH_3CCl_3 have been removed, indicates that the ratio Fe:Cl is 1:3.0 and that $FeCl_3$ is slightly active. (Table 6.XVIII). Analysis of the $H^{36}Cl$, before and after the reaction shows that the specific activity of the $H^{36}Cl$ has decreased. The decrease in the specific activity of the $H^{36}Cl$ is due to the production of inactive HCl and to exchange between $H^{36}Cl$ and wet $FeCl_3$.

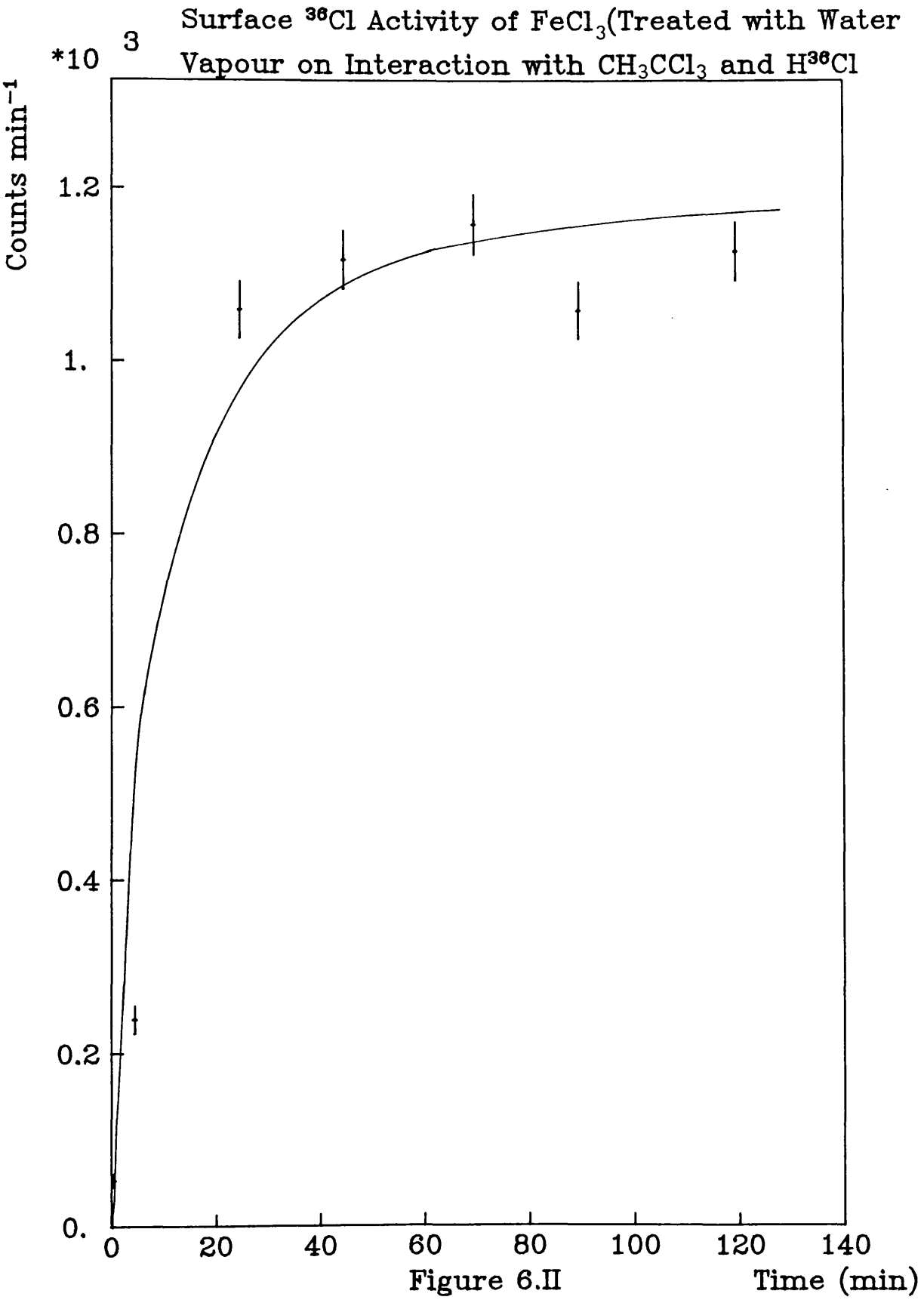

Surface ^{36}Cl Activity of $FeCl_3$(Treated with Water Vapour on Interaction with CH_3CCl_3 and $H^{36}Cl$
*10 3
Counts min^{-1}
1.2
1.
0.8
0.6
0.4
0.2
0.
0
20
40
60
80
100
120
140
Time (min)

Figure 6.II

SPECIFIC ACTIVITIES FROM THE INTERACTION OF $FeCl_3$ (TREATED WITH WATER VAPOUR) WITH CH_3CCl_3 AND $H^{36}Cl$.

Sample	Specific Activity Counts $(5min)^{-1}mg^{-1}$
Initial $H^{36}Cl$, counted as $Ag^{36}Cl$	843 ± 40
Final $H^{36}Cl$, counted as $Ag^{36}Cl$	621 ± 28
$FeCl_3$, counted as $Ag^{36}Cl$	33 ± 3

TABLE 6.XVIII

6.2.6. INTERACTION OF $FeCl_3$ with CH_3CCl_3 AND $H^{36}Cl$ MONITORED BY EXCHANGE METHOD B.

In this method the interaction between $H^{36}Cl$ and a solution of $FeCl_3$ in CH_3CCl_3 is monitored at intervals by removing aliquots of $H^{36}Cl$. If ^{36}Cl exchange occurs the specific activity of $H^{36}Cl$ will decrease and incorporation of activity into $FeCl_3$ will be observed. The specific activity of $H^{36}Cl$ will decrease, however, due to the production of inactive HCl caused by the $FeCl_3$-catalysed dehydrochlorination of CH_3CCl_3.

When $H^{36}Cl$ (0.2196g; 6.02 mmol) is admitted to a solution of $FeCl_3$ (0.1622g; 1.00 mmol) in 50ml of CH_3CCl_3 the specific activity of $H^{36}Cl$ drops with time until after 6h the values obtained are too small to be meaningful. (Table 6.XIX). Analysis of the $FeCl_3$ after the removal of HCl and CH_3CCl_3 indicates that the ratio Fe:Cl is 1:3.0 and that $FeCl_3$ is inactive.

SPECIFIC ACTIVITIES OF $H^{36}Cl$ FROM THE INTERACTION OF $FeCl_3$ WITH CH_3CCl_3 and $H^{36}Cl$.

Specific Activity of $H^{36}Cl$ Counted as $Ag^{36}Cl$ Counts $(10min)^{-1}$ mg^{-1}	Time h.
456 ± 21	0
53 ± 3	3
12 ± 1	6
6 ± 1	24
7 ± 1	48

TABLE 6.XIX

6.2.7. INTERACTION OF $FeCl_3$ WITH STABILIZED CH_3CCl_3.

$FeCl_3$ does not completely dissolve in stabilized CH_3CCl_3 but forms an orange-brown solution which contains some undissolved solid. After three weeks, however, the

solution is yellow-green and contains no undissolved solid. Infrared spectra of the vapour from a mixture of $FeCl_3$ in CH_3CCl_3 show no evidence for the production of HCl and GLC analysis of the solvent indicates that no vinylidene chloride is formed in solution.

6.2.8. OXIDATION STATE OF IRON IN $FeCl_3$|STABILIZED CH_3CCl_3 AND $FeCl_3$|STABILIZED CH_3CCl_3|HCl.

The oxidation state of iron from $FeCl_3$|stabilized CH_3CCl_3 and $FeCl_3$|stabilized CH_3CCl_3|HCl was examined by spectrophotometric analysis (cf. 2.3.3.) and the electronic spectra of the solutions recorded at various stages during the reaction.

Spectrophotometric analysis of these solutions indicate that Fe^{II} is formed in both systems. (Table 6.XX).

Fe^{II} ANALYSIS OF $FeCl_3$|STABILIZED CH_3CCl_3 AND $FeCl_3$|STABILIZED CH_3CCl_3|HCl.

System	% Fe^{II} Present of Total Iron
$FeCl_3$| STABILIZED CH_3CCl_3	14.4
$FeCl_3$|STABILIZED CH_3CCl_3| HCl	12.6

TABLE 6.XX

Spectroscopic examination of the $FeCl_3$|stabilized CH_3CCl_3 system shows that $FeCl_4^-$ is present in solution after 14h. The $FeCl_3$|stabilized CH_3CCl_3|HCl system shows that $FeCl_4^-$ is present in solution after only 1h. $FeCl_4^-$ can be detected in both solutions after three weeks.

The reduction of $FeCl_3$ to Fe^{II} suggests that chlorination of the solvent may occur, though it is also possible that the stabilizers added to CH_3CCl_3 could be responsible for the production of Fe^{II} and $FeCl_4^-$. A stabilizer such as CH_3CN would lead to the production of both these species. The presence of the stabilizers will have an effect on the exchange reaction between a mixture of $FeCl_3$ in stabilized CH_3CCl_3 and $H^{36}Cl$ as the production of $FeCl_4^-$ will lead to the incorporation of activity into the solid.

6.2.9. INTERACTION OF $FeCl_3$ WITH STABILIZED CH_3CCl_3 AND $H^{36}Cl$ MONITORED BY EXCHANGE METHOD A.

When $H^{36}Cl$ (0.0887g; 2.43 mmol) and (0.2327g; 1.74 mmol) are admitted to $FeCl_3$ (0.1630g; 1.01 mmol) and the resulting distribution of ^{36}Cl activity monitored by two GM tubes, the count rate from the gas plus solid increases with time and that from the gas alone decreases. The difference in count rates gives the ^{36}Cl activity of $FeCl_3$ and the variation of this

with time is shown in Figure 6.III. The surface activity is unaffected by the removal of $H^{36}Cl$ and stabilized CH_3CCl_3 from the gas phase though it decreases slightly after overnight pumping. Analysis of the remaining solid, after $H^{36}Cl$ and stabilized CH_3CCl_3 have been removed, indicates that the ratio Fe:Cl is 1:3.6 and that the solid is slightly active. (Table 6.XXI).

SPECIFIC ACTIVITIES OF THE REACTANTS FROM THE INTERACTION OF $FeCl_3$ WITH STABILIZED CH_3CCl_3 AND $H^{36}Cl$.

Sample	Specific Activity Counts $(5min)^{-1}mg^{-1}$
Initial $H^{36}Cl$, counted as $Ag^{36}Cl$	154 ± 8
Final $H^{36}Cl$, counted as $Ag^{36}Cl$	126 ± 6
Remaining Solid, counted as $Ag^{36}Cl$	20 ± 2

TABLE 6.XXI

Analysis of the $H^{36}Cl$, before and after the reaction shows that the specific activity of the $H^{36}Cl$ has decreased.

Surface ^{36}Cl Activity of the solid from the Interaction of $FeCl_3$ with STABILIZED CH_3CCl_3 and $H^{36}Cl$

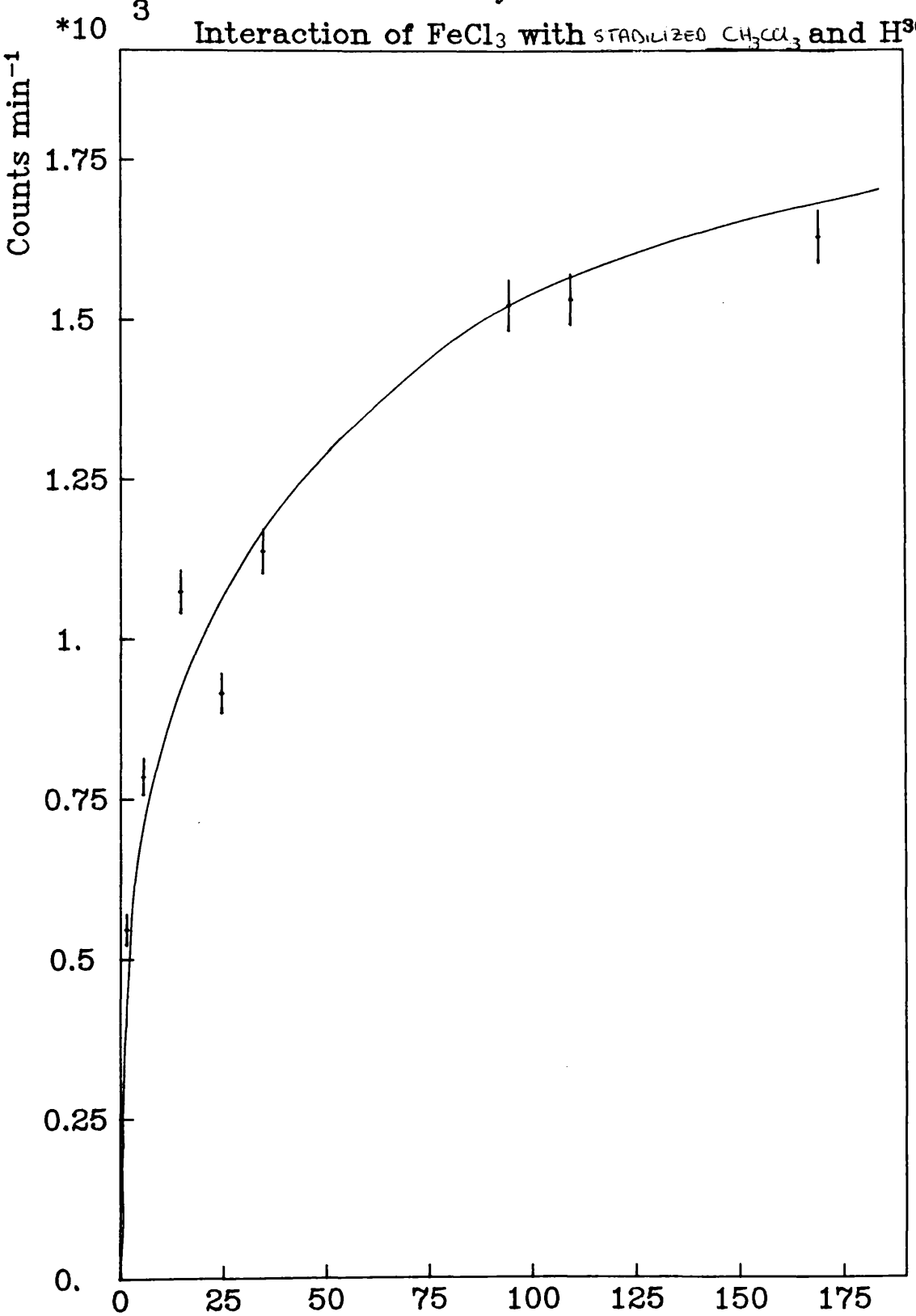


Figure 6.III

This exchange reaction is caused by the stabilizers present in CH_3CCl_3 since under identical conditions no exchange was observed in the $FeCl_3$|unstabilized CH_3CCl_3|$H^{36}Cl$ system

6.2.10. INTERACTION OF $FeCl_3$ WITH STABILIZED CH_3CCl_3 AND $H^{36}Cl$ MONITORED BY EXCHANGE METHOD B.

When HCl (0.2847g; 7.81 mmol) is admitted to a mixture of $FeCl_3$ (0.1622g; 1.00 mmol) in 50ml of stabilized CH_3CCl_3, the pressure of $H^{36}Cl$ in the vessel drops so rapidly that even after 1h. it is not possible to remove any $H^{36}Cl$. On removal of the solvent, analysis of the remaining solid indicates that the ratio Fe:Cl is 1:4.6 and that the solid is active.

These results indicate that not only do the stabilizers added to CH_3CCl_3 prevent the formation of HCl but they consume any HCl added to the system.

6.3. DISCUSSION.

Iron(III) chloride catalyses the dehydrochlorination of 1,1,1-trichloroethane to produce HCl and vinylidene chloride. The amount of vinylidene chloride formed in a mixture of $FeCl_3$ in CH_3CCl_3 is decreased by the addition of HCl, H_2O and CH_3CN though it is increased if the mixture is stored in the dark. Since light obviously plays a role in the production of vinylidene

chloride, mixtures of $FeCl_3$ in CH_3CCl_3 were analysed for the presence of Fe^{II}. The amount of Fe^{II} present is unaffected by the addition of HCl or CH_3CN, decreased by the addition of H_2O and totally inhibited when the mixture is stored in the dark.

It has been suggested[5] that the dehydrochlorination of 1,1,1-trichloroethane involves a carbonium ion intermediate as shown in scheme 6.I and this would

$$CH_3CCl_3 + FeCl_3 \rightarrow [CH_3CCl_2^+ + FeCl_4^-]$$

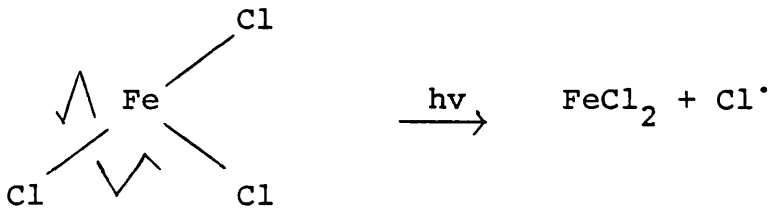
$$[CH_3CCl_2^+ + FeCl_4^-] \rightarrow CH_2CCl_2 + FeCl_3 + HCl$$

Scheme 6.I.

result in the $FeCl_4^-$ ion being formed in solution. This, however, is inconsistent with the spectroscopic investigation which shows no evidence for the formation of $FeCl_4^-$ in mixtures of $FeCl_3$ in CH_3CCl_3 unless water is present. The formation of the tetrachloroferrate ion would lead to exchange occurring between a mixture of $FeCl_3$ in CH_3CCl_3 and $H^{36}Cl$ as outlined in Scheme 6.II. Although the specific activity of the $H^{36}Cl$ added to a mixture of $FeCl_3$ in CH_3CCl_3 decreases, this is due to the production of inactive HCl from the dehydrochlorination of CH_3CCl_3 and no exchange occurs. When this reaction is repeated using $FeCl_3$, which had previously been treated with water vapour, exchange occurs to some extent. Presumably this is due to the reaction between

wet $FeCl_3$ and $H^{36}Cl$ discussed in Chapter 5.

The formation of Fe^{II} in these solutions suggests that there is a photochemical reduction of Fe^{III} to Fe^{II} with concomitant production of a chlorine radical (Scheme 6.III).



Scheme 6.III

The chlorine radical formed could react with CH_3CCl_3 and provide an alternative mechanism for the production of $CH_2 = CCl_2$ (Scheme 6.IV). The reaction

$$Cl^{\cdot} + CH_3CCl_3 \rightarrow HCl + {}^{\cdot}CH_2CCl_3$$

$${}^{\cdot}CH_2CCl_3 \rightarrow CH_2 = CCl_2 + Cl^{\cdot}$$

$$Cl^{\cdot} + {}^{\cdot}CH_2CCl_3 \rightarrow CH_2ClCCl_3$$

Scheme 6.IV

between $FeCl_3$ and CH_3CCl_3, however, was not examined for the presence of any other organochloro compounds. The production of vinylidene chloride caused by the photochemical reduction of Fe^{III} to Fe^{II} explains both the

formation of vinylidene chloride and Fe^{II} in mixtures of $FeCl_3$ in CH_3CCl_3. Since the dehydrochlorination of CH_3CCl_3 is an equilibrium reaction (eq. 6I) the reduction in the amount of vinylidene chloride formed in solution when HCl is added to a mixture of $FeCl_3$ in CH_3CCl_3 is probably due to the excess HCl present disturbing this equilibrium. When H_2O is added to a mixture of $FeCl_3$ in CH_3CCl_3 both the amount of CH_2CCl_2 and Fe^{II} produced decreases. Presumably the water reacts with $FeCl_3$ to give $[Fe(H_2O)_4Cl_2^+]$-$[FeCl_4^-]$ (cf. Table 5.I) leaving less $FeCl_3$ available for the photochemical pathway and thus reducing the amount of vinylidene chloride and Fe^{II} produced. It has been shown[90], however, that the reaction between CH_3CCl_3 and hydrated iron(III) chloride results in the formation of acetic acid, (Eq. 6.II) though

$$CH_3CCl_3 + 2H_2O \xrightarrow{FeCl_3} CH_3CO_2H + 3HCl \quad .....Eq.\ 6.II$$

as the $FeCl_3$ becomes anhydrous, dehydrochlorination becomes predominant and vinylidene chloride is formed. When CH_3CN is added to a mixture of $FeCl_3$ in CH_3CCl_3, no vinylidene chloride is formed although Fe^{II} is present. Presumably this is due to solvolysis of the $FeCl_3$ by CH_3CN which leads to the production of $[Fe^{II}(CH_3CN)_6][FeCl_4]_2$ and explains the presence of Fe^{II} in solution. When a mixture of $FeCl_3$ and CH_3CCl_3 is stored in the dark, the photochemical reduction ceases

and no Fe^{II} is detected. Surprisingly the amount of vinylidene chloride formed is greatly increased which indicates that there is another route to the formation of vinylidene chloride which does not involve the chlorine radical. Molecular $FeCl_3$ must be present when a mixture of $FeCl_3$ in CH_3CCl_3 is stored in the dark. A possible explanation for the increased vinylidene chloride concentration in this mixture is that the CH_3CCl_3 is adsorbed on coordinatively unsaturated sites on the surface of the $FeCl_3$ which causes slight ionization of the CH_3CCl_3 and results in loss of HCl. The reaction between $FeCl_3$ and a mixture of $H^{36}Cl$ and CH_3CCl_3 (cf. 6.2.4) indicated that some adsorption took place between $FeCl_3$ and either CH_3CCl_3 or $CH_2 = CCl_2$. When water, CH_3CN or another stronger Lewis base is added to a mixture of $FeCl_3$ in CCl_3CH_3, they cause solvolysis of the $FeCl_3$ thus decreasing the amount of vinylidene chloride formed.

In summary, iron(III) chloride catalyses the dehydrochlorination of 1,1,1-trichloroethane both by the photochemical reduction of Fe^{III} to Fe^{II} which produces a chlorine radical and by the interaction of vinylidene chloride with molecular $FeCl_3$. The light initiated reaction probably results not only in the formation of vinylidene chloride but also in other organochloro compounds. Molecular $FeCl_3$, therefore, appears to be the most efficient dehydrochlorination

catalyst since most vinylidene chloride is produced when no species are present to solvate $FeCl_3$ and the reaction is performed in the dark.

CHAPTER SEVEN

CHAPTER 7

CONCLUSIONS

36-Chlorine exchange is not observed between anhydrous $FeCl_3$ and anhydrous $^{36}Cl_2$ which indicates that the Fe(III)-Cl bond is not labile towards Cl_2 under anhydrous conditions. Under these conditions $^{36}Cl_2$ is merely adsorbed by the $FeCl_3$. ^{36}Cl exchange occurs between $FeCl_3$ and $^{36}Cl_2$ in acetonitrile as a result of chlorination of the solvent. The reaction involves solvolysis of $FeCl_3$ and an $Fe^{III}|Fe^{II}$ redox cycle. $Fe(CH_3CN)_6^{2+}$ is oxidised by chlorine in acetonitrile and therefore shows similar behaviour to $FeCl_3$. The lifetime of the cycle is limited due to the production of HCl which reacts with the cationic Fe^{III} species forming the redox inactive tetrachloroferrate ion.

These results suggest that the catalytic ability exhibited by $FeCl_3$ in chlorination reactions could be caused by Lewis bases reacting with $FeCl_3$ to form a catalytically active species. In the heterogeneous reaction the adsorption of Cl_2 by molecular $FeCl_3$ could weaken the Cl-Cl bond thus causing it to react more readily with an alkene or alkyne.

36-Chlorine exchange is not observed between anhydrous $FeCl_3$ and anhydrous $H^{36}Cl$ under heterogeneous conditions. ^{36}-Cl exchange and adsorption of $H^{36}Cl$

both occur in the presence of small quantities of water but it is considered that these processes involve $[Fe(H_2O)_4Cl_2][FeCl_4]xH_2O$ rather than $FeCl_3$. No exchange is observed between $H^{36}Cl$ and $FeCl_4^-$ which implies that exchange involves $H^{36}Cl$ and $[Fe(H_2O)_4Cl_2]^+$.

Hydrochlorination of chloroalkanes in the presence of $FeCl_3$ and H_2O, as a co-catalyst, presumably involves adsorption of HCl by $[Fe(H_2O)_4Cl_2]^+$ which weakens the HCl bond. It has been noted elsewhere that if the concentration of water is too high or if solvents such as acetonitrile are used then hydrochlorination is inhibited. This is presumably due to the fact that both these solvents will promote the formation of $FeCl_4^-$. The ability of $FeCl_3$ to function as a hydrochlorination catalyst is not due to molecular $FeCl_3$ but to the species present when $FeCl_3$ is dissolved in certain solvents. The choice of solvent is very important as the species formed on reaction with $FeCl_3$ must be capable of causing ionization of the HCl.

In the dehydrochlorination of chloroethanes catalysed by $FeCl_3$, the catalytically active species appears to be molecular $FeCl_3$. In these reactions the chloroalkane is adsorbed by the molecular $FeCl_3$. Donor solvents inhibit dehydrochlorination as they reduce the amount of molecular $FeCl_3$ present.

In dehydrochlorination reactions, $FeCl_3$ is often dissolved in solvents such as nitroethane and 1-nitropropane though unless excess solid iron(III) chloride is present the reaction is totally inhibited. A possible explanation for the observed increase in the rate of dehydrochlorination is that the species formed when the co-catalyst solvates the $FeCl_3$ could adsorb the HCl produced in the reaction. The molecular $FeCl_3$ present adsorbs the chloroalkane and thus the rate of dehydrochlorination increases.

Future work in this area could investigate the reactions of $FeCl_3$ with non-aqueous solvents and the ability of the species formed to function as catalysts. The preparation of $Fe^{36}Cl_3$ would enable the lability of the Fe(III)-Cl bond to be more thoroughly investigated. The preparation of labelled chlorohydrocarbons and a thorough investigation of their behaviour with $FeCl_3$, both with and without the presence of a co-catalyst, would yield much useful information on the mechanisms involved in these reactions.

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